

CONJUGATING BINARY SYSTEMS FOR SPACECRAFT THERMAL CONTROL - FINAL REPORT

January 1989

(NASA-CR-183608) CONJUGATING BINARY SYSTEMS
FOR SPACECRAFT THERMAL CONTROL Final Report
(Lockheed Missiles and Space Co.) 112 p

N89-21023

CSCI 22B

Unclas

G3/18 0204512

Contract NAS8-36199

Prepared for

**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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FOREWORD

This report documents the work performed on the material search aspects of Contract NAS8-36199 "Conjugating Systems for Spacecraft Thermal Control." The work dealing with development of realist demonstration unit was reported previously in the following report:

Design, Fabrication, Check-Out, and Operation of the NASA-MSFC Thermal Control System Technology Test Bed", J.C. Hammet, Lockheed Report LMSC-HEC TM D0660309, December 1986.

In addition, the following paper, prepared during the course of this contract and attached as Appendix B, presents a comprehensive overview of CB technology accomplished up to January 1987.

"Conjugating Binary Solutions for Spacecraft Thermal Control", P.G. Grodzka and J.W. Owen, International Symposium on Thermal Problems in Space-Based Systems, 13 - 18 December 1987, Flavio Dobran and Murray Imber, Editors, ASME Publication HTD-Vol. 83, ASME, New York, New York.

The work accomplished under Task 6 is provided under separate cover as Appendix C, "Aeroassist Flight Experiment Carrier Vehicle Preliminary Stress Analysis."

The Marshall Space Flight Center (MSFC) Contracting Officer's Representative for this study is Mr. Jim Owen, EP44.

ACKNOWLEDGEMENTS

Test data on Candidate CB performances in the Fluid-Loop Test System (FLTS) were collected by Lori Sisk and Jeff Hammet under the direction of Bill Dean.

Sincere thanks also to Marshall Spinner for programming the computer data collection and reduction, and to Paul McCormick for invaluable general help and advise and for the design of the FLTS.

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NOMENCLATURE

CB	conjugating binary
CST	critical solution temperature
FLTS	fluid-loop test system
GN	Godfrey number
LCB	conjugating binary with a LCST
LCST	lower critical solution temperature
QST	quick screening test
TCS	thermal control systems
UCB	conjugating binary with a UCST
UCST	upper critical solution temperature

1. BACKGROUND AND INTRODUCTION

A concept for spacecraft thermal control systems (TCS) has recently emerged that depends on the heat of mixing a pair of different liquids at a critical solution temperature (CST). Liquid pairs that mix (or unmix) at a CST are called conjugating binary (CB) systems. The CB concept appears attractive for TCS because only liquid phases are involved. Thus, heat transfer problems associated with the separation of phases in the absence of gravity can be avoided.

A CB system for spacecraft heat transfer offers the advantage of significant reduction of pumping power requirements over conventional liquid Freon or coolant systems. Because of the nature of the variation of the heat capacity as a function of temperature, a CB system could also provide some self-regulating thermal control without an active control system. The total liquid character of CB systems promises significant advantages over gas-liquid two-phase systems in space. This total liquid nature also promises the avoidance of expensive zero-g flight tests and experiments of phase separation concepts. CB materials can be chosen to undergo liquid-liquid phase change over a range of desired temperatures. Some CBs even undergo two different liquid-liquid phase changes at two different temperatures. They thus offer versatility for a variety of applications.

The CB concept is quite new, requiring a number of assessments before its ultimate feasibility can be ascertained. The objective of the proposed study is to demonstrate generically the validity of the concept for spacecraft heat transfer and thermal control.

Tasks

To accomplish the objective of this contract, Lockheed was tasked with the following original tasks.

Task 1: Identify and characterize candidate CB pairs through a literature search and laboratory tests.

Task 2: Investigate the effects of additives on CST, C_p , freezing temperatures, etc.

Task 3: Develop a fluid-loop bench test CB demonstration unit and perform tests on a selected candidate CB pairs.

Task 4: Develop a fluid loop demonstration unit compatible with, and for testing in, the MSFC Sunspot I Thermal Vacuum Test Chamber using surplus Skylab hardware, and assist MSFC in testing.

Task 5: Investigate the applicability of CB technology/concept to space flight vehicles.

Task 6: Prepare a preliminary design of a demonstration flight test article for Space Shuttle testing.

Task 7: Prepare a preliminary design of CB system for Space Station testing.

Task 8: Document the results.

Tasks 5 and 7 were never funded and thus a modified task statement was developed in 1988. The modified tasks are presented below.

Task 1: The contractor is to fully characterize candidate CB pairs through a literature search along with a laboratory test program. Among the properties which must be characterized versus temperature are the viscosity, density, specific heat, and thermal conductivity. Additionally, the CST, heat of mixing, freezing point, toxicity, and corrosiveness of each CB pair must be determined.

Task 2: The contractor is to investigate the sensitivity of fluid properties to additives which tend to enhance or alter CB system characteristics. The results may be used for tailoring of the CST, effective specific heat, freezing temperature, etc.

Task 3: The contractor is to develop a fluid loop bench test unit to demonstrate CB system performance in the fluid dynamic environment. This unit minimally must consist of a pump, heat source, heat sink, and adequate instrumentation. Data which must be quantitatively recordable include flow rate, temperature rise, heat input, and pump power. Additionally, qualitative observations should be possible to characterize mixing, foaming, separation, or other physical characteristics of the system. The contractor is to utilize this facility to test each of the candidate CB pairs.

Task 4: The contractor is to develop a demonstration unit compatible with thermal vacuum test environments, suitable for testing in an MSFC thermal vacuum chamber. The major components for the unit, pumps, valves, radiators, heat exchanges, and coldplates, shall be provided by MSFC.

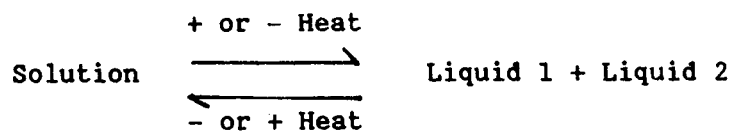
Task 5: The contractor is to provide a written report documenting the development effort and describing the status of work completed to date.

Task 6: Unchanged

This final report completes the studies conducted under Task 1, 2, and 3. Task 4 has been completed and the results reported under the following document: "Design, Fabrication, Check-Out, and Operation of the NASA-MSFC Thermal Control System Technology Test Bed," LMSC-HEC TM D066039, dated December 1986. Task 5 is satisfied with the final report. Task 6 is reported as Appendix C to this report (under separate cover).

2. METHODOLOGY FOR IDENTIFYING AND SCREENING CANDIDATE CBs

The CB concept of increasing the heat capacity of a heat transfer fluid over a small temperature interval depends on utilizing the heat effect accompanying the phase transformation



A review of the principles involved and a report on an experimental demonstration of the concept are given in Refs. 1 through 3.

As indicated in previous reports, practical CBs need to generally meet as closely as possibly the following criteria:

- Appropriate Critical Solution Temperature (CST)
- High Heat of Mixing at the CST
- Low Viscosity
- Low Freezing Temperature
- High Boiling Temperature
- Stability to Repeated Cycling
- Little or no Supercooling or Superheating
- High Flash Point
- Non-Corrosive and Non-Toxic.

The first problem addressed in the present search for practical CBs is how to predict the critical solution temperature (CST) of a given CB because only very limited CST data exist in the literature. After reviewing a mass of papers on solubility parameters, a paper that gives some practical guidance for choosing liquid pairs was found. In this paper, "Solvent Selection via

Miscibility Number" (CHEMTECH, June 1972, pp. 359-363), Norman B. Godfrey reports the results of miscibility tests with some 400 different organic solvents. He was able to assign a miscibility number, M, to each solvent which generally reflected its lipophilicity (affinity for oil-like substances). He found that if the M-number of two liquids differ by 15 units or less, the two liquids are miscible in all proportions at 25 C. If the M-number difference is 16, the two liquids have a critical solution temperature between 25 C and 75 C. An M-number difference of 17 or more indicates immiscibility or a critical solution temperature above 75 C. Unfortunately Godfrey did not include water, which is of prime interest to the present study, in his M-number scheme. The failure to include water in the M-number scheme is unfortunate, and further study of the literature was pursued to see if there might be some correlation between Godfrey's M-numbers and the more generally familiar Hildebrand parameter, δ_o . The Hildebrand parameter is currently broken down into three parts: especially for polar materials, i.e.,

$$\delta_o^2 = \delta_d^2 + \delta_p^2 + \delta_H^2$$

where the subscripts d, p, and H reflect the contributions due to dispersion forces (d), polar forces (p), and hydrogen bonding (H). A comparison of δ_o values with M-number indicate a generally loose inverse relationship, i.e., the higher the δ_o value, the lower the M-value number. The δ_o of water is, unfortunately, anomalously high (23.4) and hence a prediction of M-number for it risky. For example, off hand one would tend to assign water an M-number of 0. On this basis triethylamine (TEA, M = 26) and water should be immiscible at up to a temperature of approximately 75 C. They are, of course, miscible at about 18 C. This one case, however, may be the exception to the rule as miscibility could generally be predicted by means of the M numbers.

On the basis of the literature and Godfrey's M number paper, a selection of liquids was obtained for experimentation. These are given in Table 1 along with M values.

Table 1 EXPERIMENTAL LIQUIDS

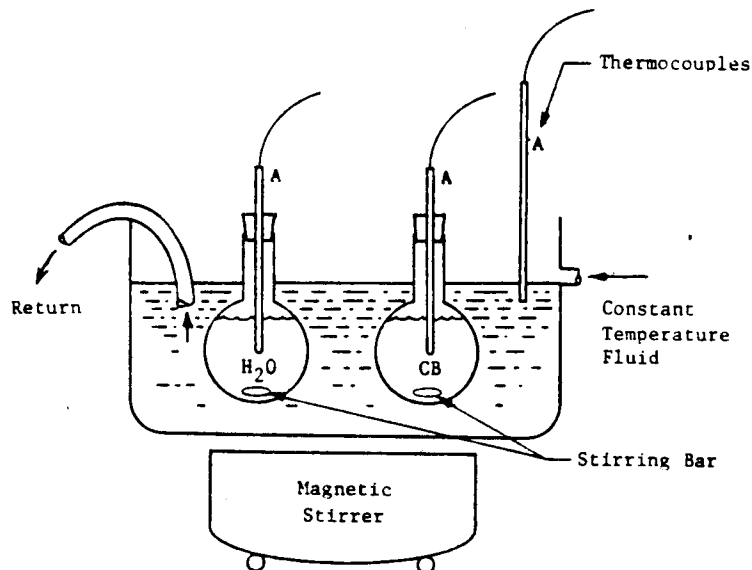
Abbrevi- ation	Liquid	Godfrey Number	Abbrevi- ation	Liquid	Godfrey Number
AA	Acetic Acid	14	AN	Aniline	12
AAC	Acetylacetone	12,18	ECEL	2-Ethoxy Ethanol (Ethyl Cellosolve)	14
AC	Acetone	15, 17	EG	Ethylene Glycol	2
BA	n-Butyl Acetate	22	MCEL	Ethylene Glycol Monomethyl Ether (Methyl Cellosolve)	13
BUA	Butylamine		EP	1-Ethylpiperidine	
BCAR	Butyl Carbitol (Diethylene Glycol Monobutyl Ether)		FORM	Formamide	3
BCEL	Butyl Cellosolve (Ethylene Glycol Monobutyl Ether, 2-Butoxyethanol)	16	DPK	4-Heptane (Butyrone, Dipropylketone)	23
BE	Butyl Ether	26	HP	Heptane	29
BCHO	Butyraldehyde		HX	1-Hexanol	17
ISOB	Isobutyric Acid	16	LUT	2, 6 Lutidine	
NBOH	n-Butyl Alcohol	15	MSA	Methanesulfonic Acid	4
TBOH	Tert. Butyl Alcohol (2-methyl-2-propanol)		MOXAA	Methoxyacetic Acid	8
BL	γ -Butyrolactone	10	2ISOP	Diisopropylamine	
CS2	Carbon Disulfide	26	NMF	N-Methyl Formamide	
CHX	Cyclohexane	28	NMP	N-Methyl Pyrrolidone	13
CP	Cyclopentane		NEP	N-Ethyl Pyrrolidone	
CLEOH	2-Chloroethanol	11	CHP	N-Cyclohexyl- 2-Pyrrolidone	
2CLE	Dichloroethane Ethylene Dichloride	20	HEP	N-(2-Hydroxyethyl) -2-Pyrrolidone)	
			OC1Ph	Orthochlorophenol	16
			PYR	Pyrrole	

Table 1 EXPERIMENTAL LIQUIDS (Concluded)

Abbreviation	Liquid	Godfrey Number	Abbreviation	Liquid	Godfrey Number
112ClE	1,1,2 Trichloroethane		MEOH	Methanol	12
2CLM	Dichloromethane	20	MEK	Methyl Ethyl Ketone	17
3CLE	Trichloroethylene	20	MEA	Monoethanolamine	2
4CLE	Tetrachloroethylene (Perchloroethylene)	25	NO2M	Nitromethane	10,19
DEG	Diethylene Glycol	5	PCHO	Propionaldehyde	
DEA	Diethanolamine	1	1PROH	1-Propanol	15
DEC	Diethyl Carbonate	21	2PROH	2-Propanol	15
DEK	Diethyl Ketone	18	PA	Propyl Acetate	19
DES04	Diethyl Sulfate	12, 21	PC	Propylene Carbonate	9, 17
DMA	N, N-Dimethyl- acetamide	13	PTB	Propylene Glycol Mono-t-Butyl Ether	
DMF	Dimethyl Formamide	12	PYRI	Pyridine	16
DMOS	Dimethyl Sulfoxide	9	TEOSI	Tetraethylortho- silicate	23
EC	Ethylene Carbonate	6, 17	3BUA	Tributylamine	28
EDA	Ethylene Diamine	9	SUCC	Succinonitrile	
EOH	Ethanol	14	TEOA	Triethanolamine	2
EPICL	Epichlorohydrin	14, 19	TEA	Triethylamine	26
2EEA	2-Ethoxy Ethylacetate	15, 19	TOL	Toluene	23
2(EO)E	2-(2-Ethoxy Ethoxy) Ethanol	13	TOLA	Toluidine	

A number of simple mixing tests were run with various combinations of the liquids obtained. In these tests small, approximately equal amounts of liquids were mixed at room temperature and the heat effect noted by means of an immersed thermocouple. If the liquids mixed and gave a temperature rise, the solution was heated to see if separation would occur. If the liquids mixed and gave a temperature fall, the solution was cooled to see if separation would occur. If no mixing occurred, the contacted liquids were both heated and cooled to see if mixing would occur. In this manner a great deal was learned about classes of liquids and some new likely CBs discovered. The information obtained in this way is partially presented in Table 2. Candidate CBs selected for further screening were subjected to a quick screening test (QST) which was conceived and developed for purposes of this study. The nature of this test is as follows.

To start a test, two identical flasks are plunged into the circulating fluid, constant temperature bath as shown in the following sketch. One of the flasks contains a reference material, e.g., water, and the other the CB candidate.



AL-86-004

Note: Bath liquid feed and return ports are actually in front and back of the flasks rather than to the side as shown.

Table 2 EXPERIMENTAL TESTS OF SOLUBILITY FOR VARIOUS LIQUID PAIRS*

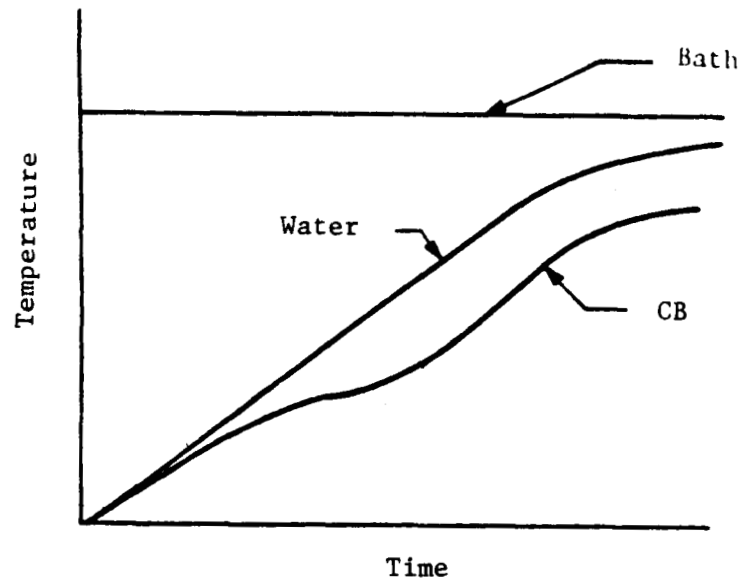
	B ₂ O	2	2	3	5	9	18	19	20	20	21	22	23	23	23	25	26	26	28	29
		ME	EG	FORM	DEG	DMSO	DEK	PA	2CLE	2CLM	DEC	BA	DPK	TEOSI	TOL	4CLE	BE	TEA	CHX	HP
EDA	9																			
AN	12	MX	MX	MX																
PRI	16	MX	MX	MX																
PYRO																				
LUT																				
EP																				
TEA	26	LCB 18	IX																	
FORM	3																			
NMF																				
DMA	12																			
DMA	13																			
SNP	13																			
NEP																				
CHP																				
HEP																				
DEC	21	I	I		UCB 40															
EC	6, 17																			
PC	9, 17	UCB 71	R	MX																
PA	19	I	UCB																	
BA	22	I																		
BL	10																			
ZEBA	15, 19																			
AA	10	MX																		
TSOB		UCB 25																		
MEA	2																			
CLETOH	11	MX																		
ETOH	14	MX																		
MeOH	12	M																		
IPROH	15																			
2PROH	15																			
TSOB	15	I																		
TSOB		MX																		
EX	17	I																		
EG	2																			
DEG	5																			
PRAL																				
BUAL																				
AC	15, 17																			
MEK	17	CB																		
DEK	18	I	I																	
DEK																				
MECL	13																			
ECCL	14																			
BCCL	16																			
2TEOE	13																			
BCAR																				
PTB																				
BE	26																			
EPICL	14, 19																			
DMSO	9																			

Abbreviations:

- I = insoluble
- M = miscible
- N = endothermic
- X = exothermic
- UCB = conjugating binary with upper critical solution temperature.
- LCS = conjugating binary with lower critical solution temperature.
- R = reacts
- loc!! = pronounced temperature rise or fall.

*Compound abbreviations as in Table 1. Numbers refer to Godfrey numbers. Other abbreviations listed above.

The temperature of both flasks and the bath during the test are monitored by means of RTDs and generally rises (assuming a LCB) as shown in the following graph.



The temperature at which the CB begins to show a significant change of rate is approximately the CST. The extent to which the CB curve continues to change slope is an indication of the heat effect involved. By measuring the slopes of the water and CB curves at the same temperatures an approximate C_p of the CB can be obtained. The rationale for this procedure is embodied in the following equality:

$$\left(mC_p \frac{dT}{dt} \right)_{CB} = \left(mC_p \frac{dT}{dt} \right)_{H_2O}.$$

By means of computer, the time-temperature data were reduced to a specific heat versus temperature plot. (The reduced data are rather ragged because stirring of the liquids is not adequate in this simple apparatus.) An averaging technique smooths the data. Some unaveraged and averaged data for the system triethylamine and water are presented in Fig. 1.

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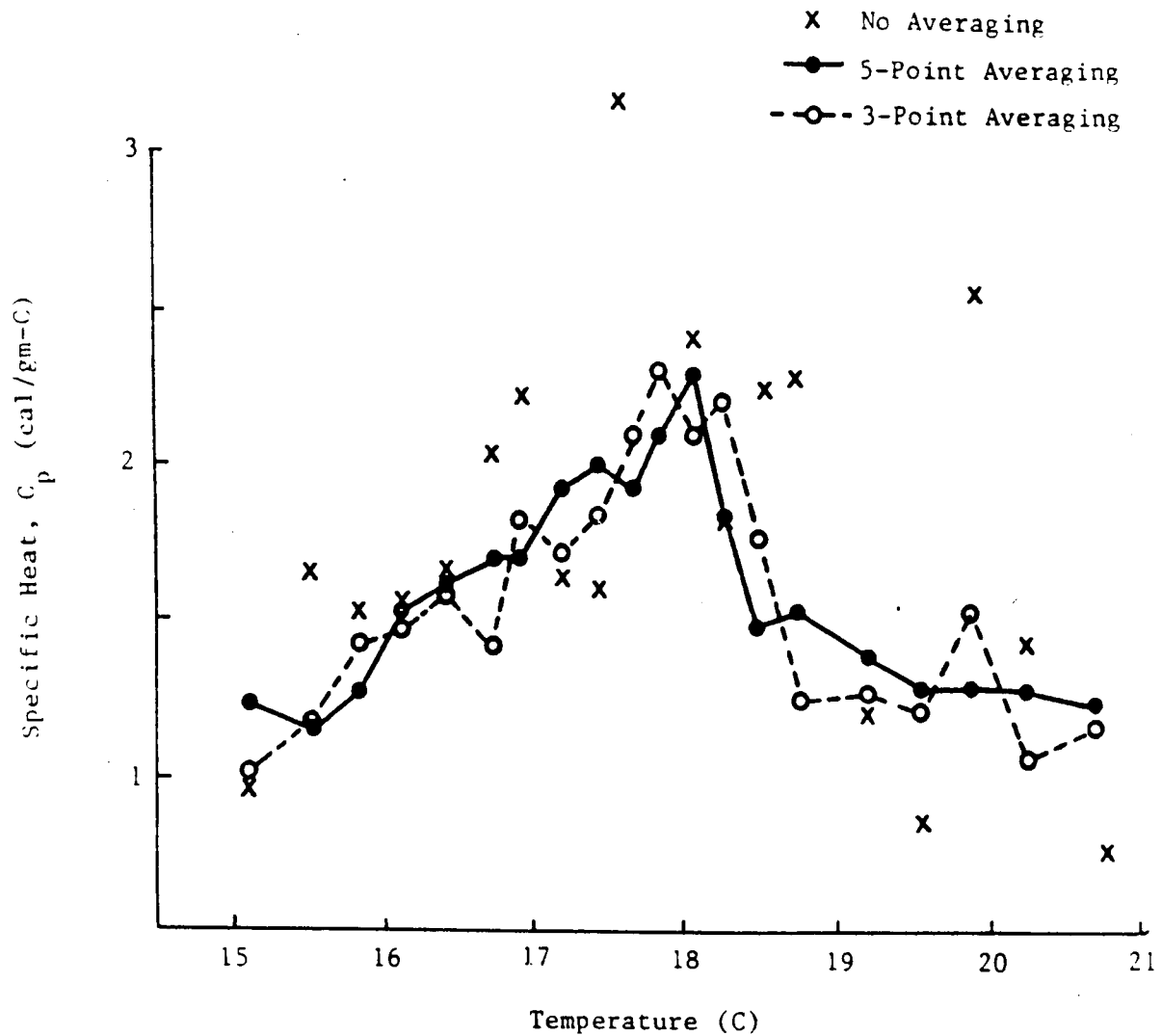


Fig. 1 QST C_p vs Temperature Data Obtained for a 37.9 Percent Triethylamine (TEA)-Water CB With and Without an Averaging Procedure

3. RESULTS OF SEARCH FOR PRACTICAL CB MATERIALS

The search took the four following directions, in the sequence shown: (1) search for liquid pairs in which both liquids are highly polar; (2) exploration of liquid pairs for which relatively high heats of mixing data are reported; (3) search for and exploration of liquid pairs that exhibit a lower CST; and (4) search for and exploration of liquid pairs in which one of the liquids is highly self-associated through hydrogen-bonding and the other a non-bonding medium such as hydrocarbon.

The results for CB solutions which were quick-screened are presented in Table 3. The starred CB systems in Table 3 are systems that were discovered in the present study. These discoveries are significant because liquid CBs with lower critical solution temperatures (LSCT) are very rare. Reported CBs with upper CSTs (USCT) outnumbered those with LCSTs by thousands.

The conclusion reached as a result of these QSTs is that practical CBs will most likely be found in the following classes of liquid-liquid interactions.

LCBs: LCBs result from bonding reactions between molecules of the component liquids. LCBs have exothermic heats of mixing which can be quite high depending on the strength of the bonds formed. Hydrogen-bonding is usually the reaction causing the mixing. In this type of reaction one liquid provides the hydrogen (acid) and the other liquid accepts the hydrogen (base). The reaction is thus an acid-base type reaction. The systems triethylamine (TEA)/water (Fig. 1) and propionaldehyde/water (Fig. 2) provide excellent examples of aqueous, hydrogen-bonding CBs. The systems triethylamine and ethylene glycol or diethylene glycol (Table 3) are non-aqueous examples. The system diisopropylamine/formamide (Table 3) probably is also a non-aqueous hydrogen-bonding CB.

Table 3 CB SYSTEMS EXPERIMENTALLY SCREENED BY QUICK SCREENING TESTS (QSTs)

CB Systems ^a	CST, C	Comment
<u>Good Performance</u>		
Epichlorohydrin/n-Heptane (43.8/56.7)	~ 20 (U)	
Triethylamine/Water (37.9/62.1)	~ 18 (L)	Solid hydrate formation at -9 C.
N-Cyclohexyl-2-Pyrrolidone/4% Saltwater (29.7/70.3)	~ 35 (L)	Solid hydrate formation at some temperature below 0 C but above -20 C.
N-Cyclohexyl-2-Pyrrolidone (0.8% NAOH Solution 170)	~ 40 (L)	
<u>Promising Performance</u>		
Propionaldehyde/Water (67.5/32.5)	~ 14 (L)	Literature reports that water solutions of aldehydes are unstable. Possibly instability could be overcome if cause was understood.
Aniline/Cyclohexane (42.5/57.5)	~ 29.5 (U)	Cyclohexane has a rather high melting point, 6.5 C. However, another suit- able hydrocarbon can undoubtedly be found, i.e., methylcyclohexane has a boiling point of 100 C and a freezing point of -126 C. The CST of this hydrocarbon and aniline is reported as 41 C.
Propylene Glycol Mono-t-Butyl Ether/ water (50/50)	(L) 8	C _p ~ 1.5 at LCST.
*Triethylamine/Ethylene Glycol (50/50)	(L) 50	C _p ~ 1.5 at LCST.
Nitromethane/n-Butanol (52/48)	(U) 15	C _p ~ 1.5 at LCST.
Diisopropylamine/Water (30/70)	(L) 26	C _p ~ 1.7 at LCST.
*Diisopropylamine/Formamide (50/50)	(L) 26	C _p ~ 1.7 at LCST. (-20 partially frozen at -20C)
Propylene Glycol Mono-t-Butyl Ether/ 10% Ethanol Water Solution(50/50)		Performance about the same as PTB/Water system but LCST raised approximately 10 C.

Table 3 CB SYSTEMS EXPERIMENTALLY SCREENED BY QUICK SCREENING TESTS (QSTs) (Concluded)

CB Systems ^a	CST, C	Comment
<u>Needing Further Investigation</u>		
Lutidine/Water (70%/30)	~ 34.06 (L) ~ 230.7 (U)	Water systems of amines or amides appear to have some sort of time dependent equilibrium establishment that causes better performance after the solution has been made up a few days than when the solution is freshly made. Not tested.
*Triethylamine/Diethylene Glycol (50/50)	(L) 85	
1-Ethylpiperidine/10% Ethanol Water Solution (30/70)	(L) 12	Excellent first run. C _p 2.7. Emulsion formation on subsequent runs.
1-Ethylpiperidine/20% Ethanol Water Solution (30/70)	(L) 16	C _p 1.7. Emulsion formation still a problem.
<u>Marginal or Poor Performances</u>		
n-Butanol/Methyl Ethyl Ketone/Water (13/35/52)	~ 20 (U)	
Propylene Carbonate/Water (59.6/40.4)	~ 71 (U)	
Methanol/Carbon Disulfide (12.5/87.5)	~ 36 (U)	
Methanol/Cyclohexane (27.6/72.4)	~ 45 (U)	
Isobutyric Acid/Water (35.2/64.8)	~ 22 (U)	
Isobutyric Acid/Ferric Chloride/Water (34.8/0.6/64.6)	~ 30 (U)	
Ethylene Diamine/Tetrachloroethylene (49.2/50.8)	~ 15.8 (U)	
n-Butanol/Methanol/Water (30.5/13/56.6)	~ 17 (U)	
N-Methyl-2-Pyrrolidone/Coolanol 20 (72.1/27.9)	~ 20 (U)	
Heptane/Methyl Cellosolve (50/50)	(U) 47	Marginal performance.
1-Ethylpiperidine/Water (30/70)	(L) 16	System forms emulsion which smears out heat effect.
Pyridine/12% KCl Solution (50/50)		Very little heat effect.

^a Numbers in parentheses are weight percents.

* Discovered in this study.

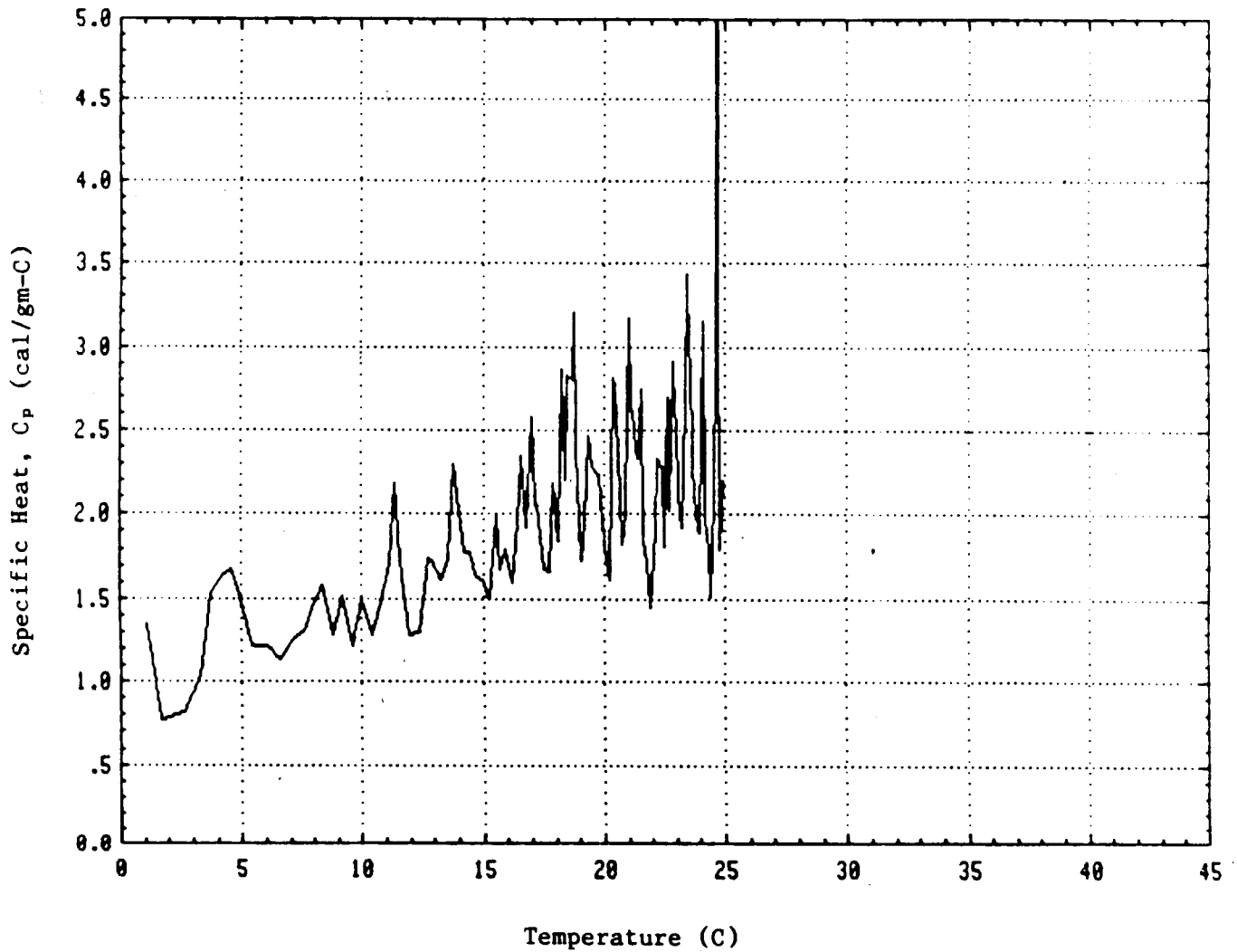


Fig. 2 QST C_p vs Temperature Data (Three Point Averaged)
for 65.7 Percent Propionaldehyde-Water CB

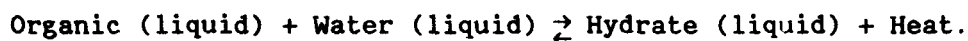
A number of literature references indicate hydrogen-bonding in combinations such as a halogenated hydrocarbon and an amide or a glycol ether or ketone. Freon 22 and dimethylacetamide, for example, exhibit astounding exothermic heats of mixing of about 45 calories per gram of solution (Ref. 4). Chloroform and compounds such as acetone and triethylamine also show spectacular heats of mixing.

Possibilities for future exploration include the following combinations:

Acid (GN)		Base (GN)	
3-Chlor-1, 2-Propanediol	(4)	Dipropyl ketone	(23)
Butyl ether	(26)	2-Aminoethanol	(2)
1, 2-Butanediol	(6)	Tributylamine	(28)

Two problems exist in trying to locate practical CBs in the LCB category. First, predictions of LCSTs on the basis of solubility parameters (GNs) are not reliable, and other predictive methodologies, which are readily applied, are lacking at this time. Second, hydrogen-bonding reactions often result in compounds that have a rather high melting points. For example, both TEA and CHP form soluble hydrates on mixing with water. The hydrate formation is the basis of the large heat effect, but unfortunately the hydrates of these particular compounds have freezing points only a few degrees below 0 C. However, other hydrates are reported in the literature that have freezing points as low as -40 C. An exploration of other promising amine, amide, aldehyde, or cellosolve aqueous systems is thus indicated.

The emergence of the role of hydrogen-bonding in CB formation raises the possibility that the following reaction may be possible.



Some literature information (Ref. 5) recently uncovered indicates that some such hydrates can dissociate without a phase separation resulting. Such a hydrate would exhibit the same sort of C_p behavior as a function of temperature

as a CB does. The exciting aspect of such a system is that there would be little question that the hydrate formation and dissociation reaction is reversible. Also the fact that the reaction takes place without a change in phase would obviate any problems with phase separation. The possibility remains to be explored.

Self-Associated, UCBs: Upper CST systems were initially dismissed rather early in the study because two test cases (isobutyric acid/water and propylene carbonate/water) showed only slight enhancement of fluid heat capacity in the quick screening tests. As our knowledge of the nature and role of hydrogen-bonding in liquid-liquid mixing grew, however, it was realized that one subcategory of this class should be explored further. This subcategory is one in which one of the liquids is highly self-associated through intramolecular hydrogen-bonding and the other acts as a neutral non-bonding carrier. In this type system, heating causes the intramolecular hydrogen-bonding to weaken, i.e., causes the self-associated liquid to become dissociated. The dissociated liquid then mixes in a normal fashion with the non-bonding carrier liquid. A prime example of this type system is the epichlorohydrin/n-heptane system. A quick screening test shows that this system (Fig. 3) indeed holds promise as a practical CB.

Other combinations within this subcategory that should be explored are amides, halogenated alcohols, and other potentially intramolecularly bonded liquids with neutral carriers.

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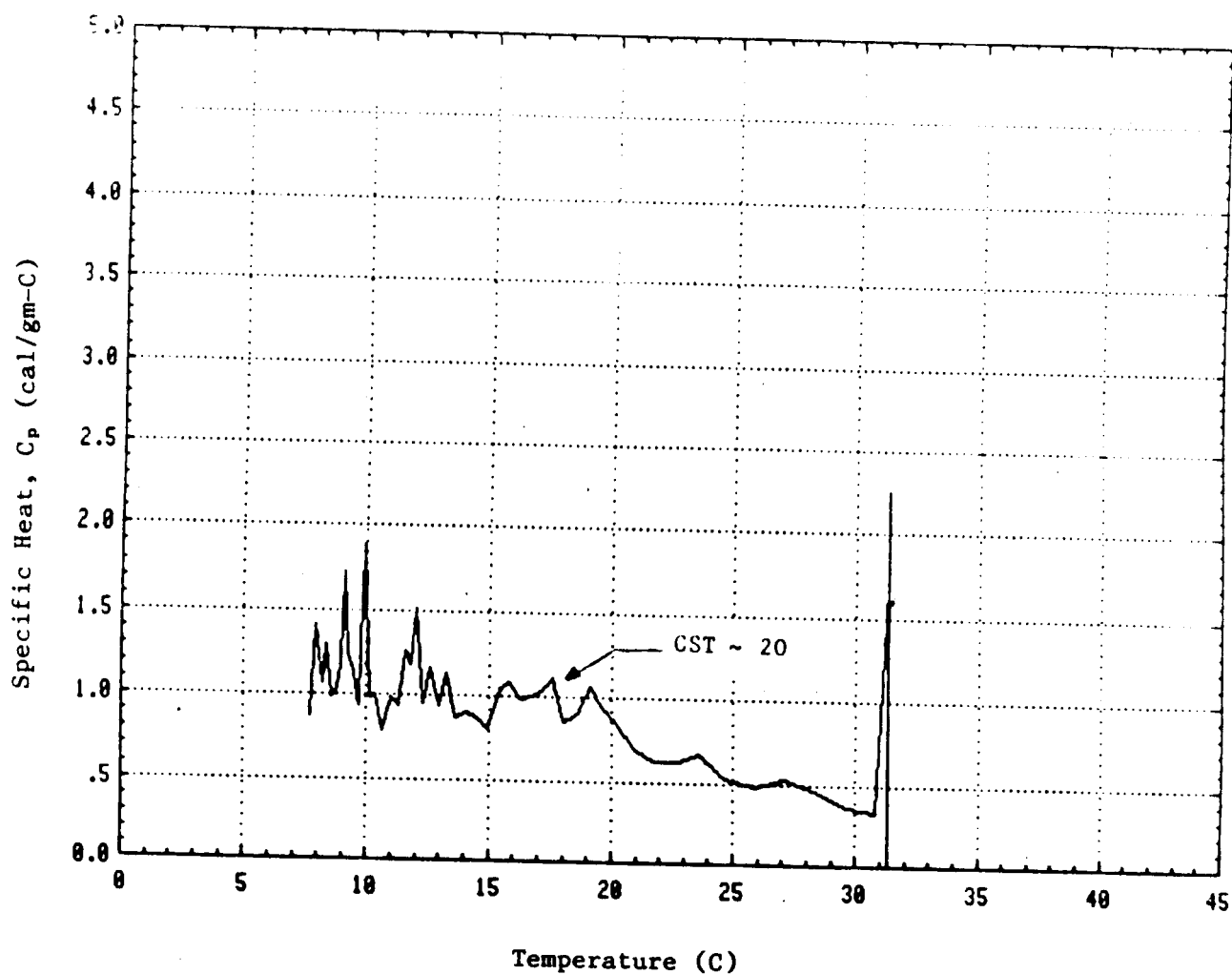


Fig. 3 QST C_p vs Temperature Data for 43.8 Percent Epichlorohydrin -n-Heptane Solution. Unaveraged Data.

4. EFFECTS OF ADDITIVES

A number of studies on the effects of various additions to various CB systems were conducted. It was found that ethanol can raise LCSTs and can, at least temporarily, alleviate emulsion problems (i.e., 1 ethylpiperdine/10% ethanol, Table 3)

Salts can either raise or lower LCSTs. The salts potassium iodide and sodium nitrate were found to raise the LCST of a N-cyclohexyl-2-pyrrolidone (CHP)/water CB. Sodium, potassium, and lithium chlorides, on the other hand, lowered the LCST. A QST of an aqueous CHP CB containing 4% KCl or LiCl, however, showed that these salts do not exert as favorable effect as does plain sodium chloride (NaCl).

Sodium chloride appeared to have a slight unfavorable effect on the performance of aqueous amine CBs. QSTs with isopropylamine and with nicotine showed a slightly lessened values of C_p . Salt also did not affect the performance of an aqueous butyl cellosolve CB.

These brief studies on additive effects indicate that further, more extensive studies are in order to gain insights on how to tailor CBs to systems requirements.

5.0 FLUID-LOOP CB TESTS

The study strategy in the present work calls for testing CB candidates identified by means of QSTs in a test loop that is a first approximation to an actual space thermal control system (Ref.1). This test system will be called the Fluid-Loop Test System (FLTS), and a system schematic is presented in Fig. 4.

The FLTS system, inherited from the prior study was substantially upgraded. Figure A-1 in Appendix A shows a photo of the latest version. This loop consists of all metal tubing rather than the Tygon used previously. It uses a variable speed gear pump, and turbine volumetric flow meter. A surplus Skylab gas-to-liquid heat exchanger is used for removing heat from the CB fluid. Heat is added to the fluid using foil electrical resistance heaters bonded to a Skylab "cold plate" heat exchanger. Power input to the fluid is determined from the measured voltage across the foil heater and the known heater resistance. All tests are conducted under a fume hood for safety. The specific heat is calculated from (1) the measured temperature rise of the CB fluid as it passes through the heat exchanger; (2) the measured flow rate; and (3) the power input. This calculation assumes steady state operation of the system at the time of each specific heat calculation. However, it has been found that an approximate steady state condition has been difficult to obtain with manual operation of the system because there are several interrelated variables to be controlled simultaneously. This is demonstrated in the data presented in Figs. A-2 and A-3. Numerous checkout and practice runs were made using water. These were needed in order to "calibrate" the system, and to get a feel for its operation, accuracy and repeatability. Once these were completed, the CB fluids were introduced, and their specific heats were measured.

A summary of the CBs tested in the FLTS is given in Table A-1 in the appendix along with the test data. The data is difficult to interpret

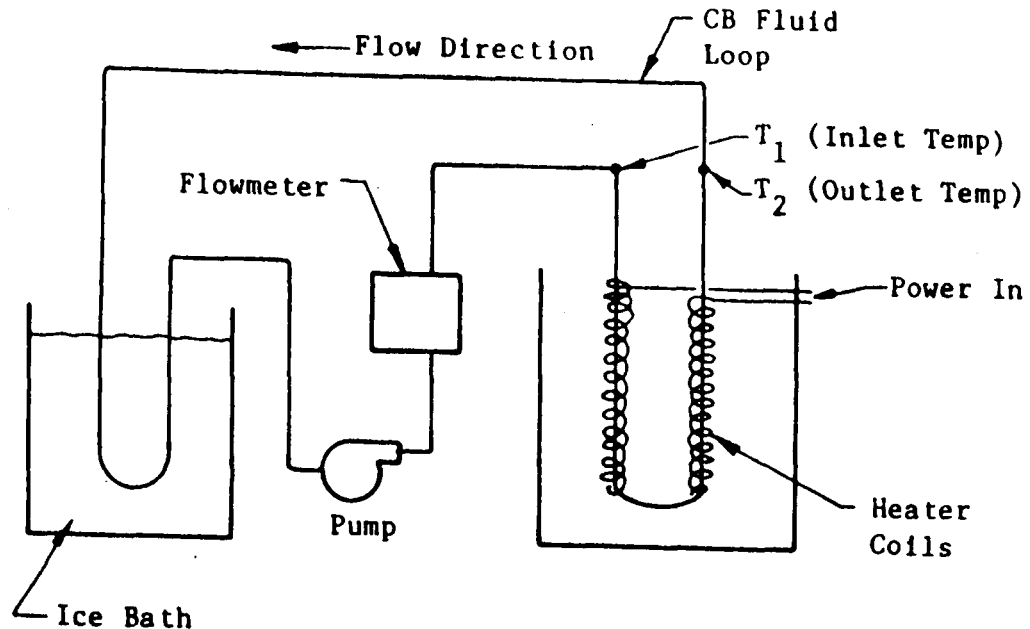


Fig. 4 FLTS Schematic

because of the rather extreme "data static" caused by the mentioned difficulty in manually adjusting of input and output temperature. Thus, it was difficult to decide if peaks in the data were actual C_p peaks or just "data static." Furthermore if the CB phase change is not perfectly reversible the C_p peak could occur at a lower or higher temperature than the equilibrium CST. The poor quality of the data allows only the following conclusions:

- CBs that showed unequivocal C_p peaks are the TEA/water and propionaldehyde/water systems.
- CBs that may have a hysteresis in the phase change include diisopropylamine/water, and propionaldehyde water.

It can be further concluded that an automatic temperature controller (to keep a constant ΔT between the inlet and outlet ports) is needed to make the present FLTS more than a very rough indicator of CB performance. In its present state it is of little use as a diagnostic tool.

6. CONCLUSIONS

The studies conducted under this contract have sharpened the direction of the materials search to liquid pairs which can form hydrogen bonds of just the right strength, i.e., strong enough to give a high heat of mixing, but weak enough to enable phase change to occur. The cursory studies performed in the area of additive effects indicate that CB performance can probably be fine-tuned by this means.

The FLTS tests of candidate CBs indicate that the systems TEA/water and propionaldehyde/water show close to ideal, reversible behavior, at least initially. The QSTs and FLTS tests, however, both suffer from rather severe "static" due either to inadequate stirring or temperature control. Thus it is not possible to adequately evaluate less than ideal CB performers. Less than ideal performers, it should be noted, may have features that make them better practical CBs than ideal performers. Improvement of the evaluation instrumentation is thus indicated.

7. RECOMMENDATIONS

The following recommendations are made for continuation of this work:

- Seek additional CBs in which the heat effect arises primarily from hydrogen-bonding
- Combine the QST and the FLTS apparatuses into a new, small FLTS which is easy to fill, take apart, empty and clean and which also is designed to have automatic temperature controls.

8. REFERENCES

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Appendix A

SUMMARY CB FLUID-LOOP TEST SYSTEM (FLTS) DATA

Fluid-Loop Test System (FLTS) test data for candidate CBs are presented in this Appendix. The FLTS used is shown in Fig. A-1. Summary CB fluids tested are presented in Table A-1. The CB test data are presented in Fig. A-2 through A-61. Summary CB characteristics are presented below.

I. 54% PROPYLENE GLYCOL MONO-t-BUTYL ETHER + 46% WATER (PTB)
(FIGS. A-2 THROUGH A-7)

This CB had an approximate CST of 64.4 F and density of 51.9 lb/ft³. The test was run at a temperature range from 45 F to 85 F for a period of 29.6 min. It has been concluded that the early C_p "peaks" are due to unsteady testing conditions rather than a phase change. Steady testing conditions were difficult to establish for this material. Since a steady state test is required for usable data, this CB candidate should be tested again.

II. 37.9% TRIETHYLAMINE + 62.1% WATER (TEA) (FIGS. A-8 THROUGH A-13)

This CB had an approximate CST of 60.8 F and a density of 71.2 lb/ft³. The test was run at temperature range from 50 F to 85 F for a period of 51.7 min. This CB candidate showed a promising C_p "peak," thus making it a good candidate for a heat transfer fluid. However, studies into the stability of this CB candidate may show that it is unstable and highly toxic. (It has an irritating odor.)

III. DIISOPROPYLAMINE + 70% WATER (FIGS. A-14 THROUGH A-19)

This CB had an approximate CST of 77 F and a density of 56.93 lb/ft³. The test was run from 70 F to 100 F for 40.0 min. This CB candidate showed no C_p "peak." Furthermore, it had a strong odor.

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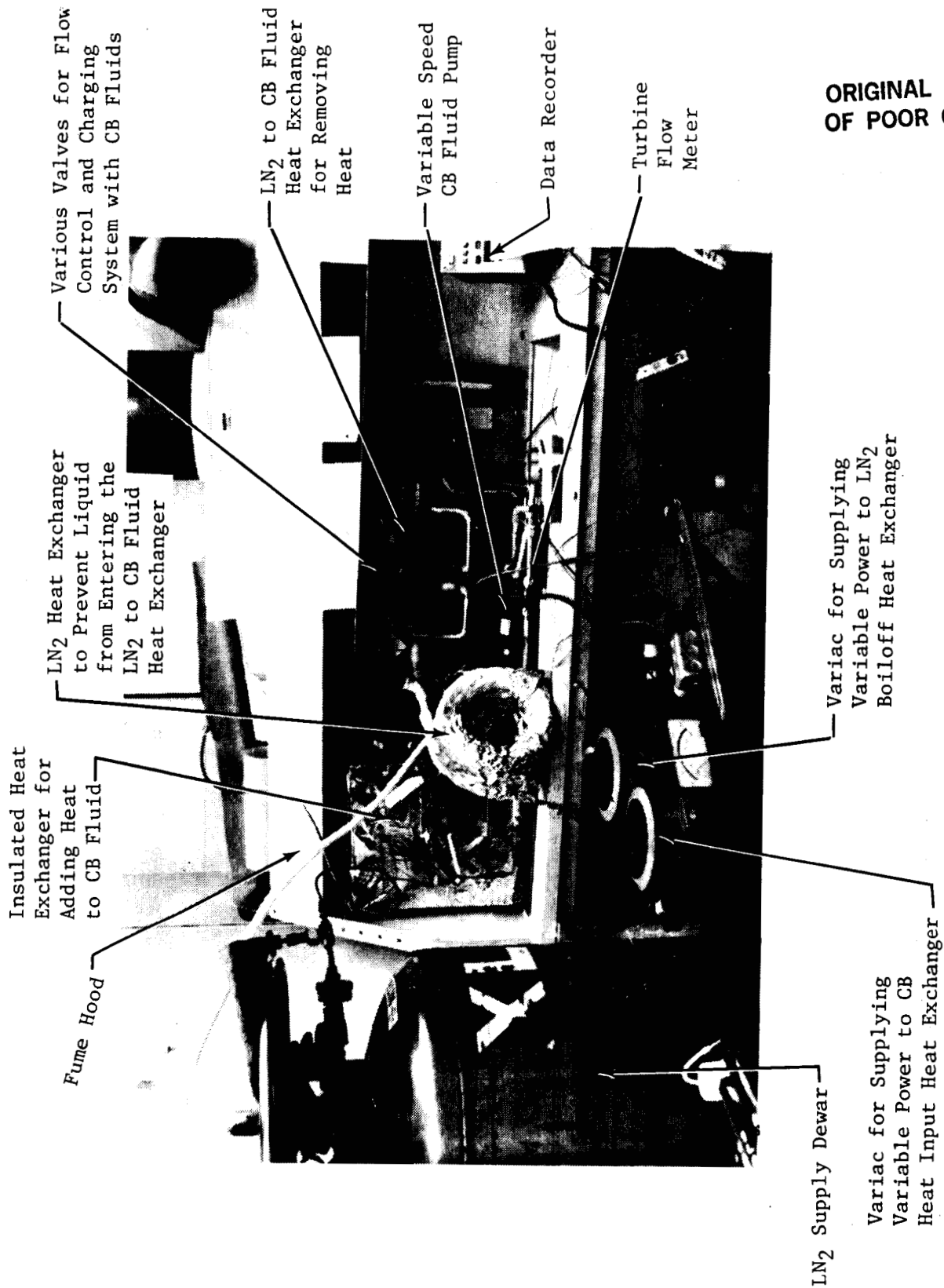


Fig. A-1 Lockheed Huntsville Fluid Loop Bench Test Setup for Testing Candidate CB Heat Transfer Fluids

Table A-1 SUMMARY OF CANDIDATE CB FLTS TESTS

Series	Run	CB	Approx. CST* (F)	Run Time (min.)	Density (lb/ft ³)	Test Comments	Fig. No.
I	3	54% Propylene Glycol Monto-t-Butyl Ether 46% Water (PTB)	64.4	29.6	51.9	Hard to get a steady state run, possibly due to nature of PTB.	A2 - A7
II	4	37.9% Triethyl-amine 62.1% Water (TEA)	60.8	51.7	71.2	Only CB which gave significant rise in C_p . Strong odor.	A8 - A13
III	5	30% Diisopropyl-amine 70% Water	77.0	40.0	56.9	Strong odor. Showed no signs of having a C_p "peak".	A14 - A19
IV	6	73% N-Methyl-Pyrrolidone	68.0	63.3	61.1	Showed no C_p "peak".	A20 - A25 27 Water
V	9	30% N-Cyclo-hexyl-2-Pyrrolidone (CHP) 70% Water	128.0	183.2	55.2	Showed no C_p "peak".	A26 - A31
VI	10	30% CHP 4% Salt 66% Water	118.0	121.7	65.2	Purity (industrial) was questionable due to discoloration.	A32 - A37
VII (a)	11	67.5% Propion-aldehyde	60.8	91.7	55.1	Hard to get steady state run due to nature of CB.	A38 - A43
(b)		32.5% Water 67.5% Propion-aldehyde 32.5% Water	60.8	33.3	55.1	Strong Odor Showed high C_p .	A44 - A49
VIII (a)	12	50% TEA 50% Ethylene Glycol	107.6	141.7	53.2	Strong odor Showed no significant C_p "peak".	A50 - A55
(b)		50% TEA 50% Ethylene Glycol	107.6	150.0	53.2		A56 - A61

* From existing literature.

IV. 73% N-METHYL PYRROLIDONE + 27% WATER (FIGS. A-20 THROUGH A-25)

This CB had an approximate CST of 68 F and density of 61.1 lb/ft³. The test run was at a temperature range from 57 F to 90 F for a period of 63.3 min. This CB also showed no significant peak. Peaks in the start of the run were concluded to be testing anomalies.

V. 30% N-CYCLOHEXYL PYRROLIDONE (CHP) + 70% H₂O (FIGS. A-26 THROUGH A-31)

This CB had an approximate CST of 123 F and density of 55.2 lb/ft³. This test was run at a temperature range from 40 F to 80 F for a period of 183.2 min. The longevity of this test is considered adequate for achieving steady state conditions. This CB showed no significant peak. This particular fluid tested well, in the fact that it achieved steady state and held it for a long period of time.

VI. 30% CHP + 4% SODIUM CHLORIDE (SALT) + 66% WATER (FIGS. A-32 THROUGH A-37)

This CB was similar to the 30% CHP + H₂O in that it tested well. This CB had an approximate CST of 118 F and a density of 65.2 lb/ft³. The test was run at a temperature range from 90 F to 135 F for a period of 121.7 min. No significant C_p "peaks" were observed. The industrial purity (the condition it arrived from chemical supplier) could introduce a question into the purity of the CB combination because the CHP was slightly discolored as compared to clear samples used before.

VII. 67.5% PROPIONALDEHYDE + 32.5% WATER (FIGS. A-38 THROUGH A-49)

This CB candidate had an approximate CST of 60.8 F and a density of 55.1 lb/ft³. The first test was run at a temperature range from 50 F to 84 F for 91.7 min. A possible C_p "peak" at 1.6 Btu/lbm-F could be concluded. The second test was run at a temperature range from 45 F to 75 for 33.33 min and a small C_p "peak" was observed at 1.5 Btu/lbm-F. Both runs

produced C_p values. This chemical, however, was hard to keep under steady state conditions and is toxic.

VIII. 50% TEA + 50% ETHYLENE GLYCOL (FIGS. A-50 THROUGH A-61)

This CB candidate had an approximate CST of 107.6 F and a density of 53.2 lb/ft³. The first test was run at a temperature range from 85 F to 140 F for a period of 141.7 min. No significant C_p peaks were observed initial "peaks" were considered due to unsteady initial conditions. The second test was run from 80 F to 135 F for a period of 150 min. Also there were no significant C_p peaks.

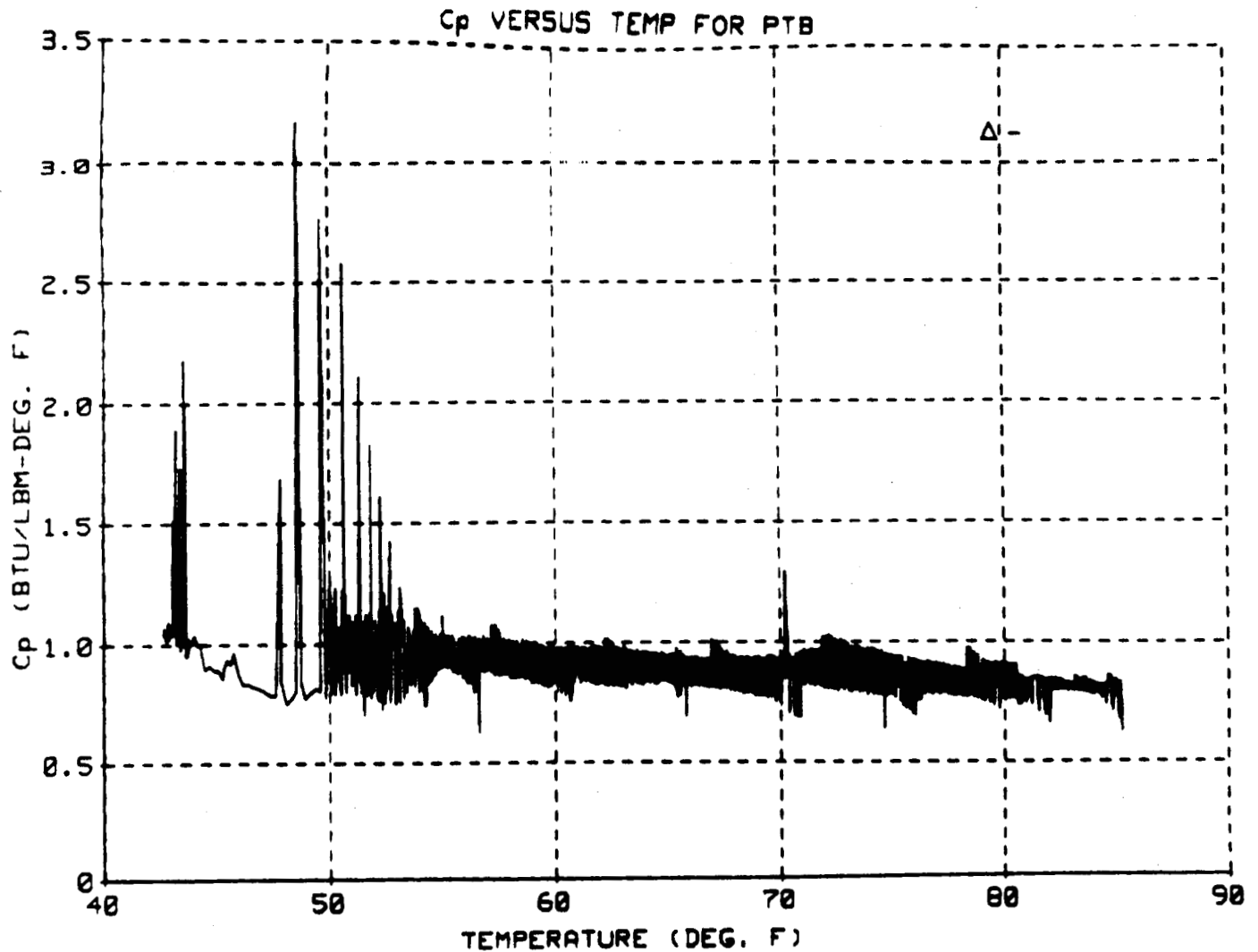


Fig. A-2 C_p vs Temperature for 54% Propylene Glycol Mono-t-Butyl Ether (PTB)/46%, 10% Ethanol/Water Solution (Run No. 3)

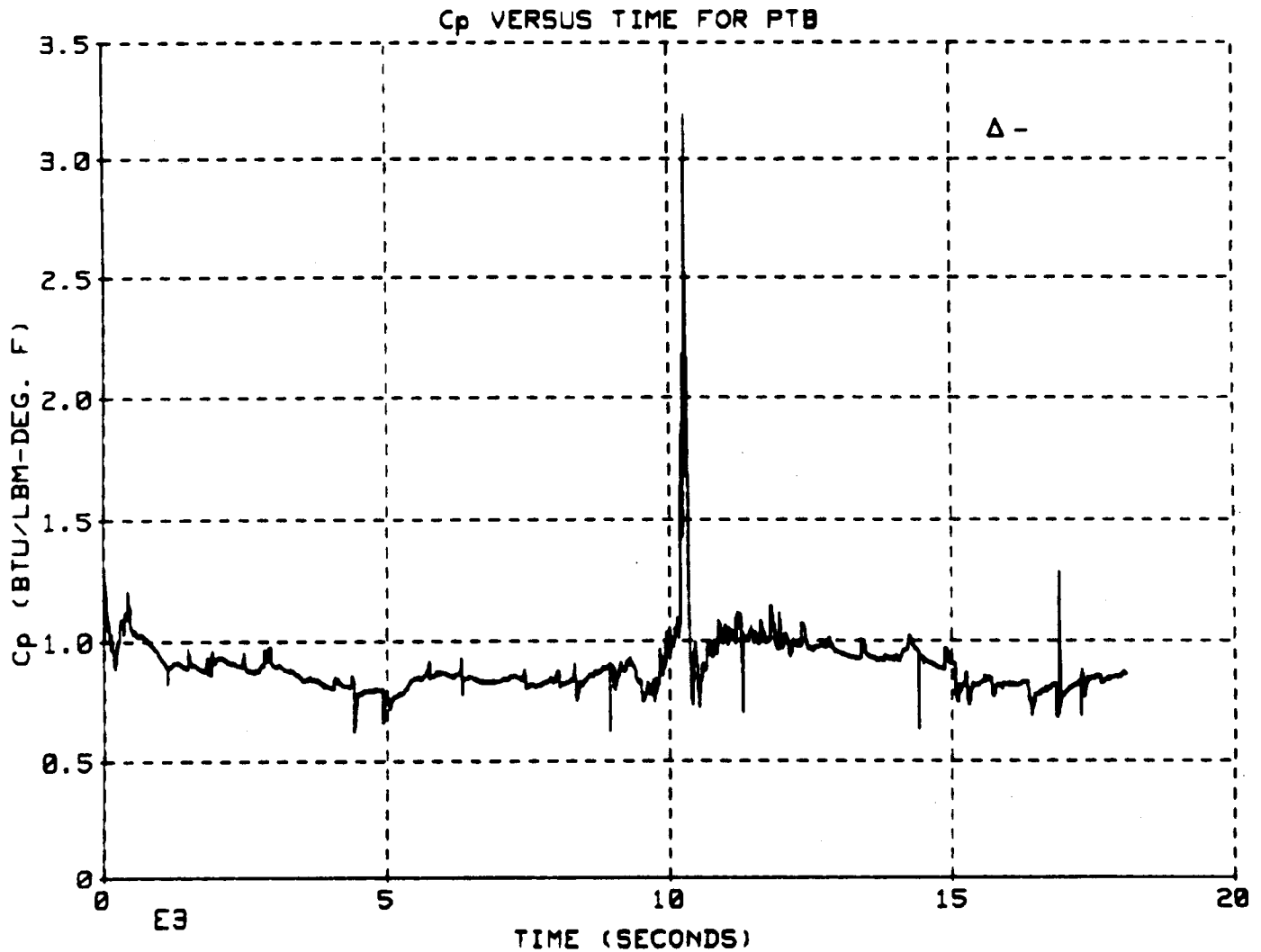


Fig. A-3 C_p vs Time for 54% Propylene Glycol Mono-*t*-Butyl Ether (PTB)/46%, 10% Ethanol/Water Solution (Run No. 3)

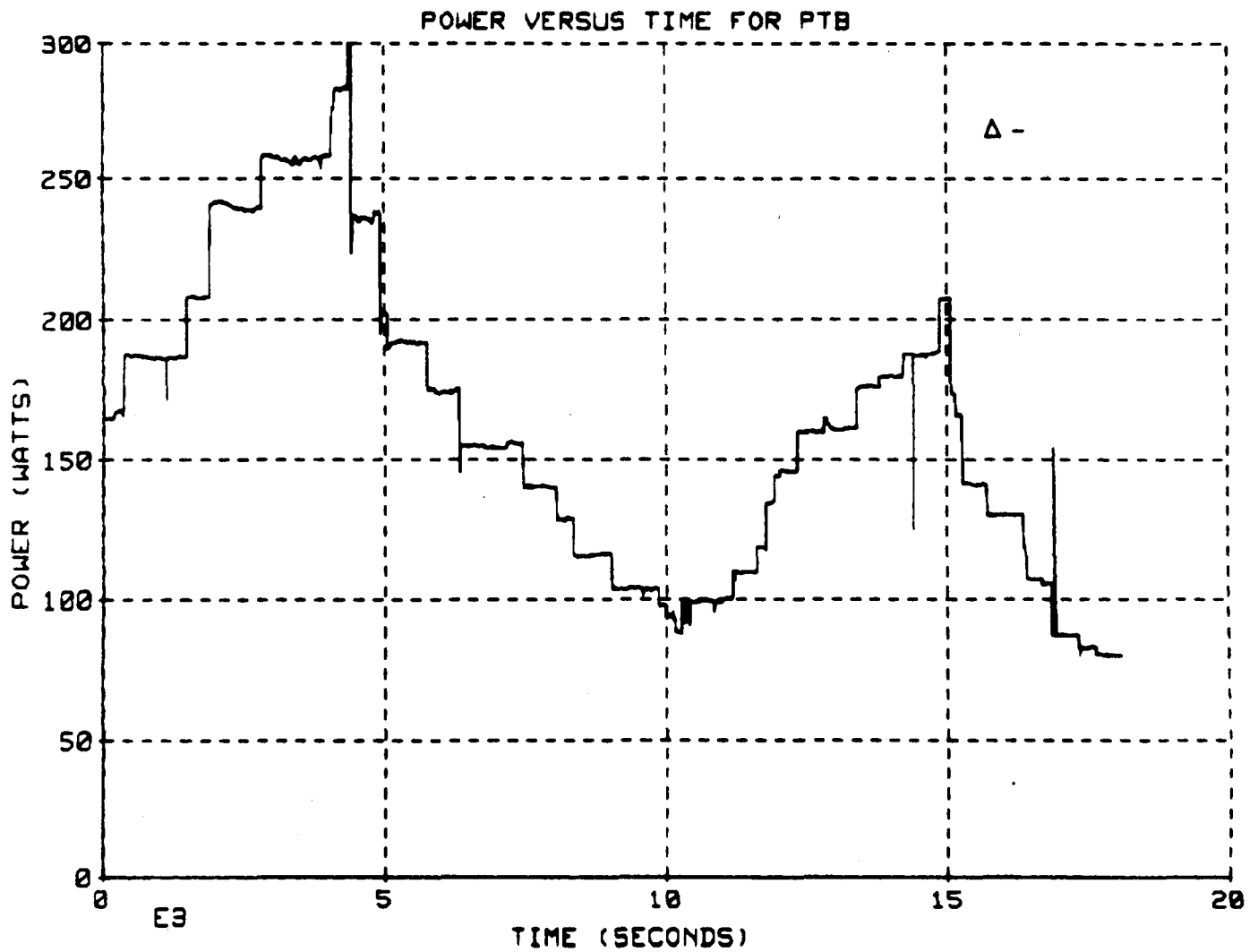


Fig. A-4 C_p vs Time for 54% Propylene Glycol Mono-*t*-Butyl Ether (PTB)/46%, 10% Ethanol/Water Solution (Run No. 3)

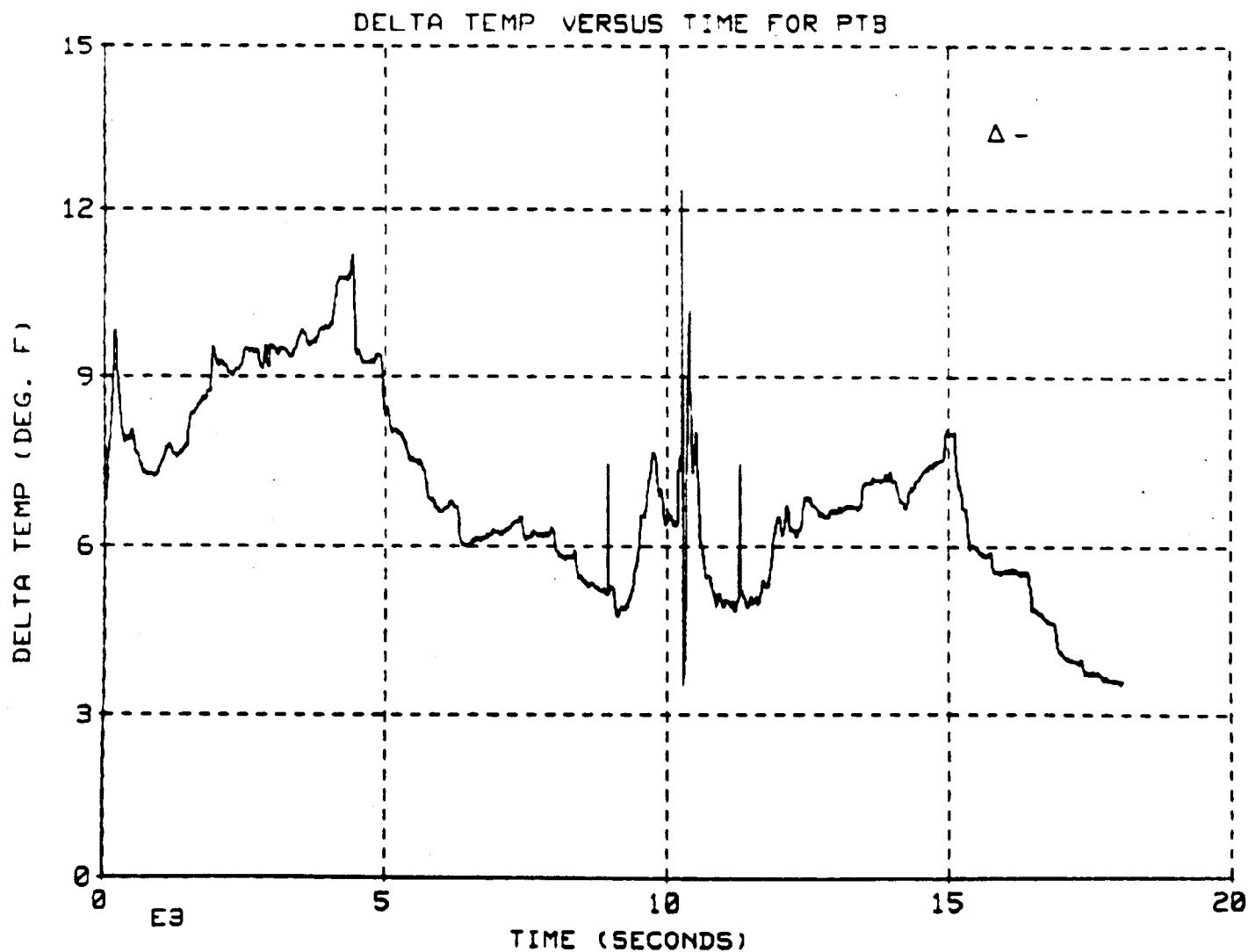


Fig. A-5 Delta Temperature vs Time for 54% Propylene Glycol Mono-*t*-Butyl Ether (PTB)/46%, 10% Ethanol/Water Solution (Run No. 3)

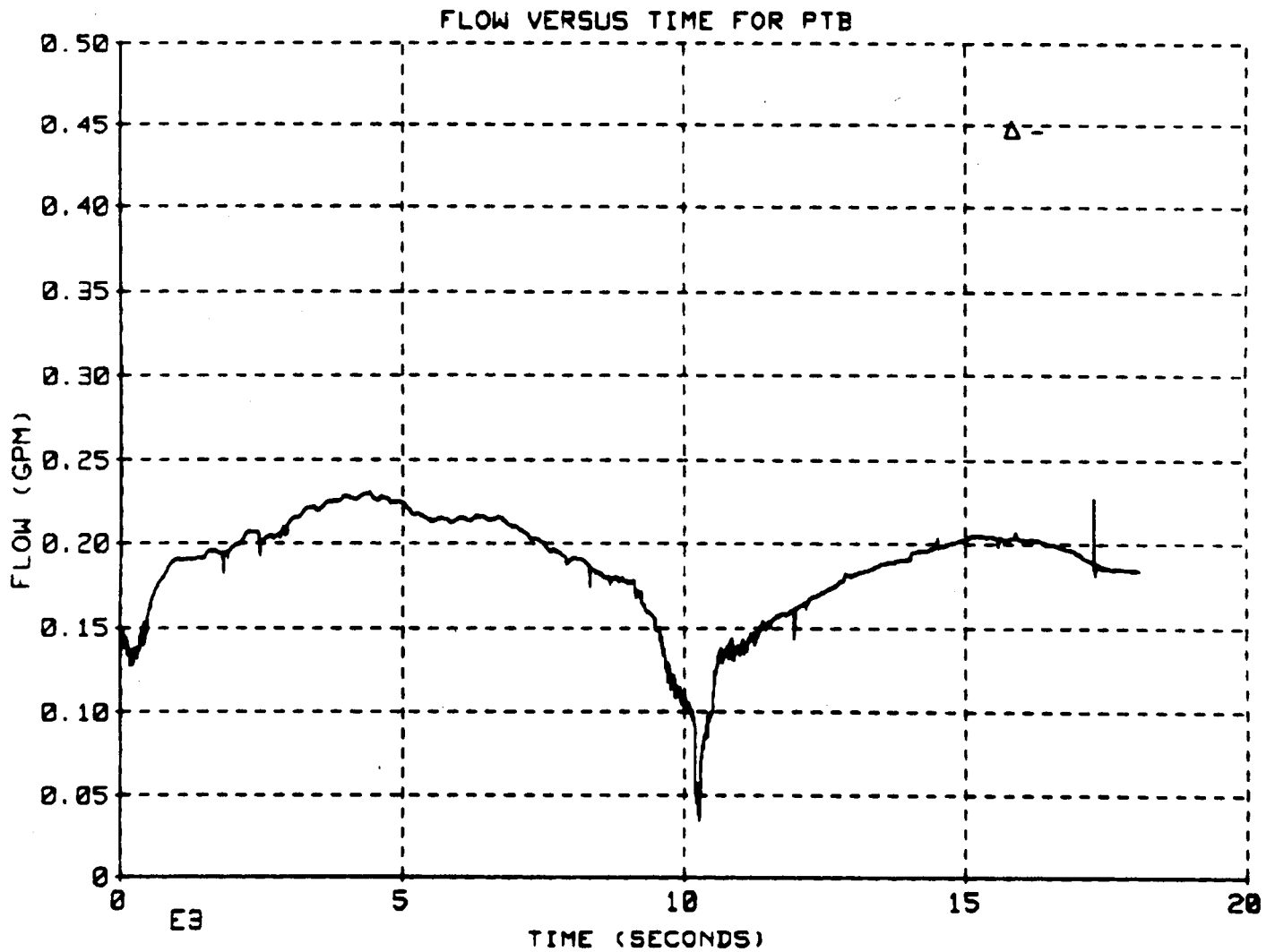


Fig. A-6 Flow Rate vs Time for 54% Propylene Glycol Mono-t-Butyl Ether (PTB)/46%, 10% Ethanol/Water Solution (Run No. 3)

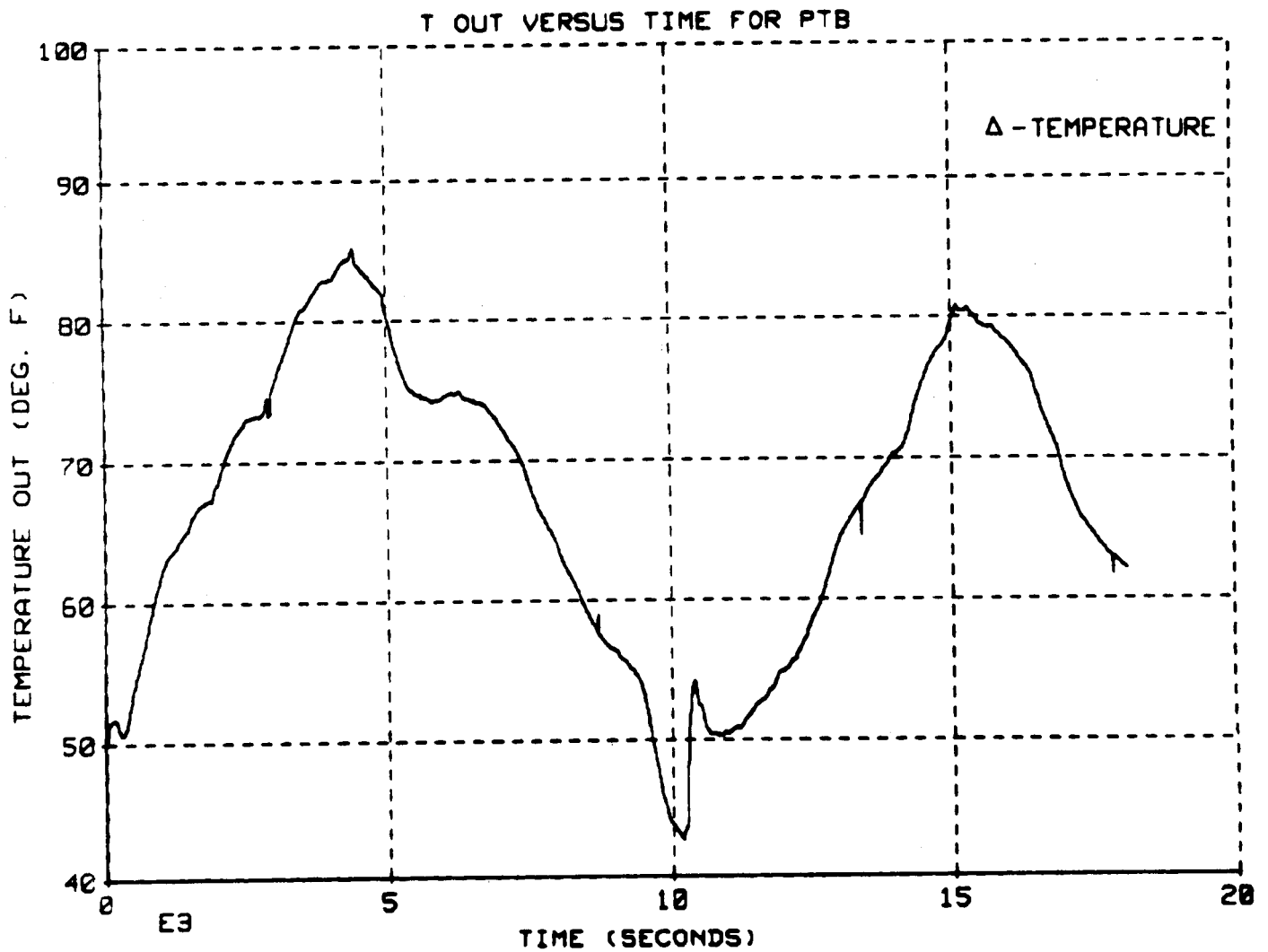


Fig. A-7 Outlet Temperature vs Time for 54% Propylene Glycol
Mono-t-Butyl Ether (PTB)/46%, 10% Ethanol/Water Solution

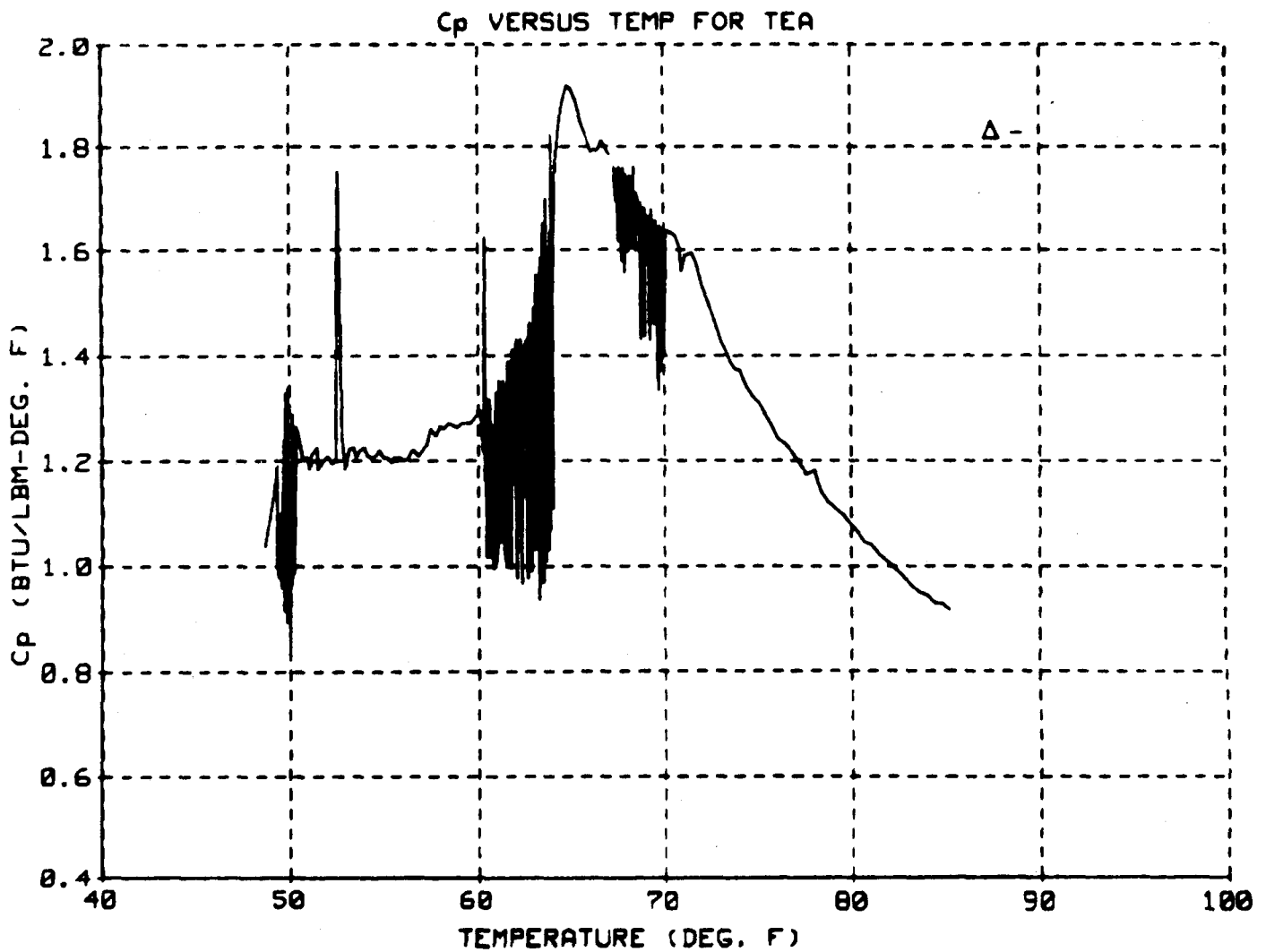


Fig. A-8 C_p vs Temperature for Triethylamine (TEA) and Water
(Run No. 4) (37.9% Triethylamine, 62.1% Water)

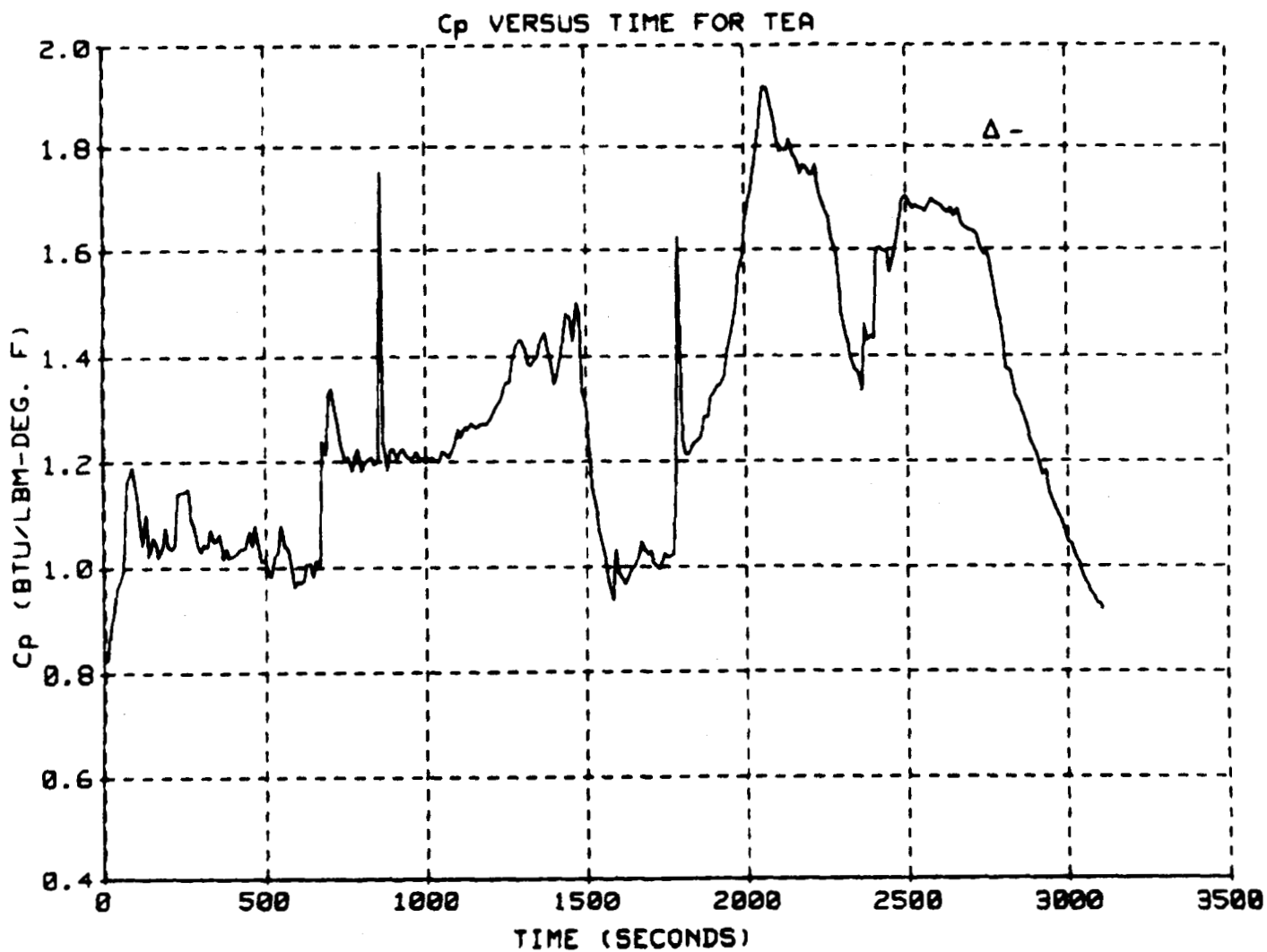


Fig. A-9 C_p vs Time for Triethylamine (TEA) (Run No. 4)
(37.9% Triethylamine, 62.1% Water)

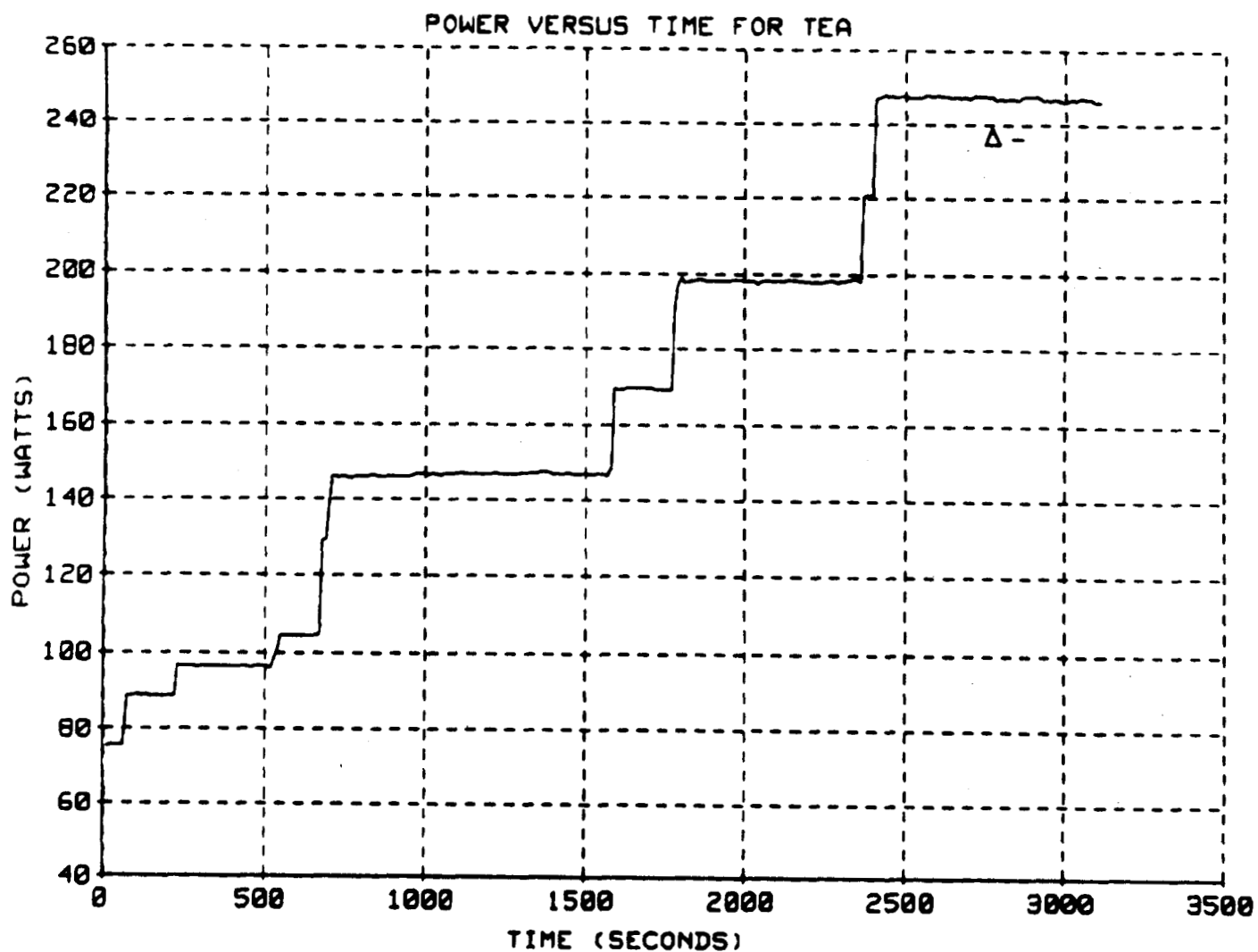


Fig. A-10 Power vs Time for Triethylamine (TEA) (Run No. 4)
(37.9% Triethylamine, 62.1% Water)

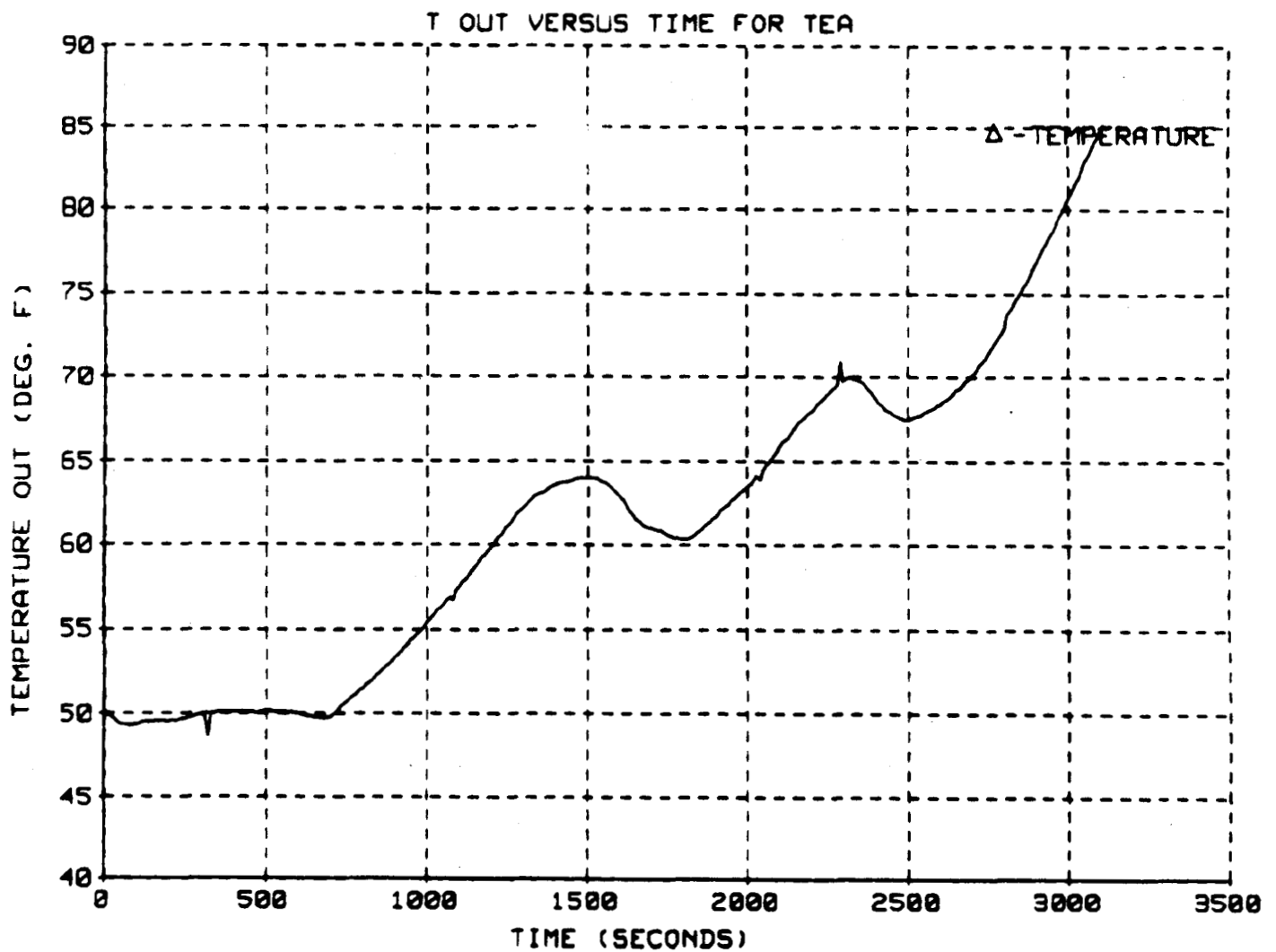


Fig. A-11 Outlet Temperature vs Time for Triethylamine (TEA) (Run No. 4)
(37.9% Triethylamine, 62.1% Water)

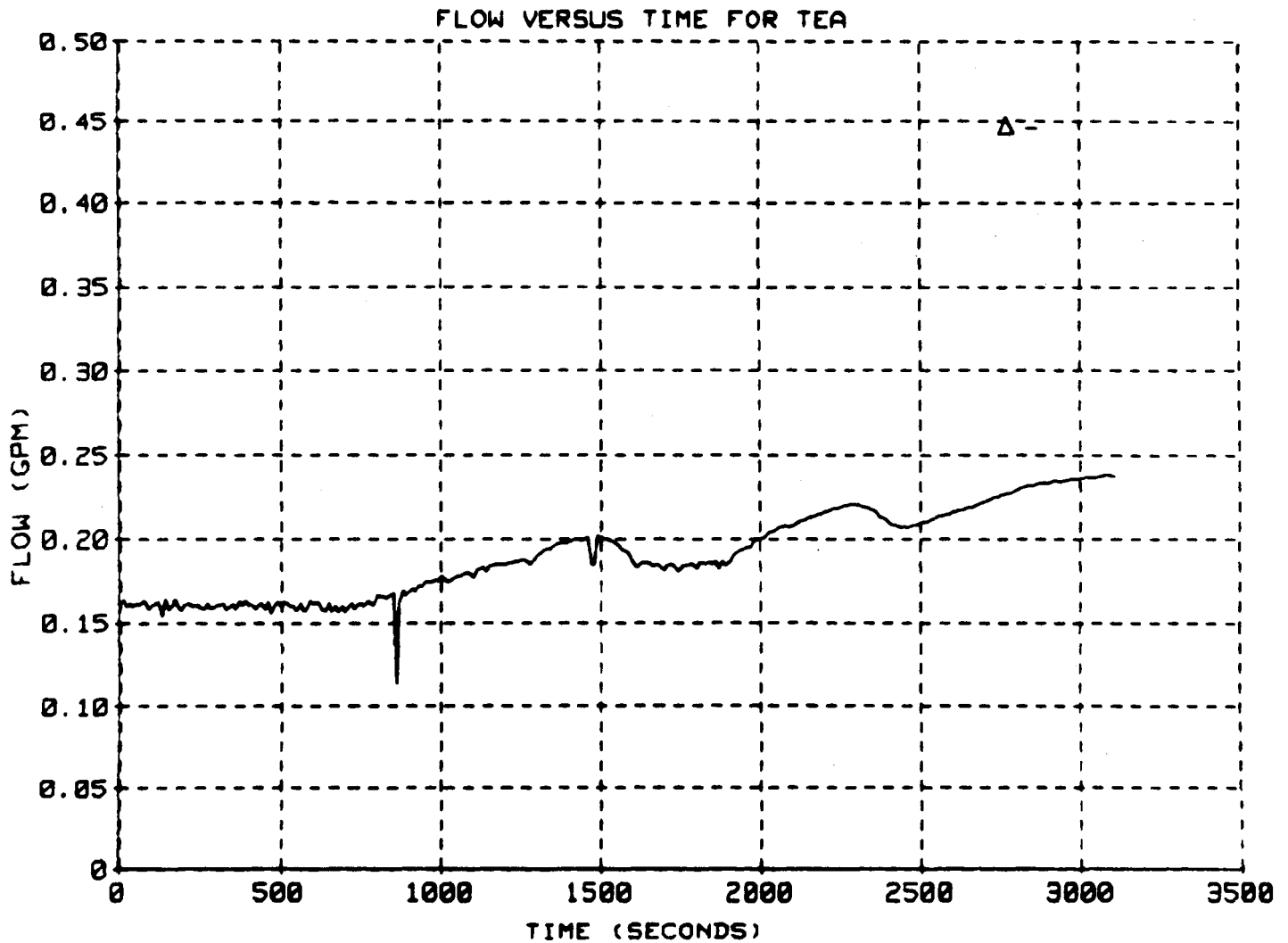


Fig. A-12 Flow Rate vs Time for Triethylamine (TEA) (Run No. 4)
(37.9% Triethylamine, 62.1% Water)

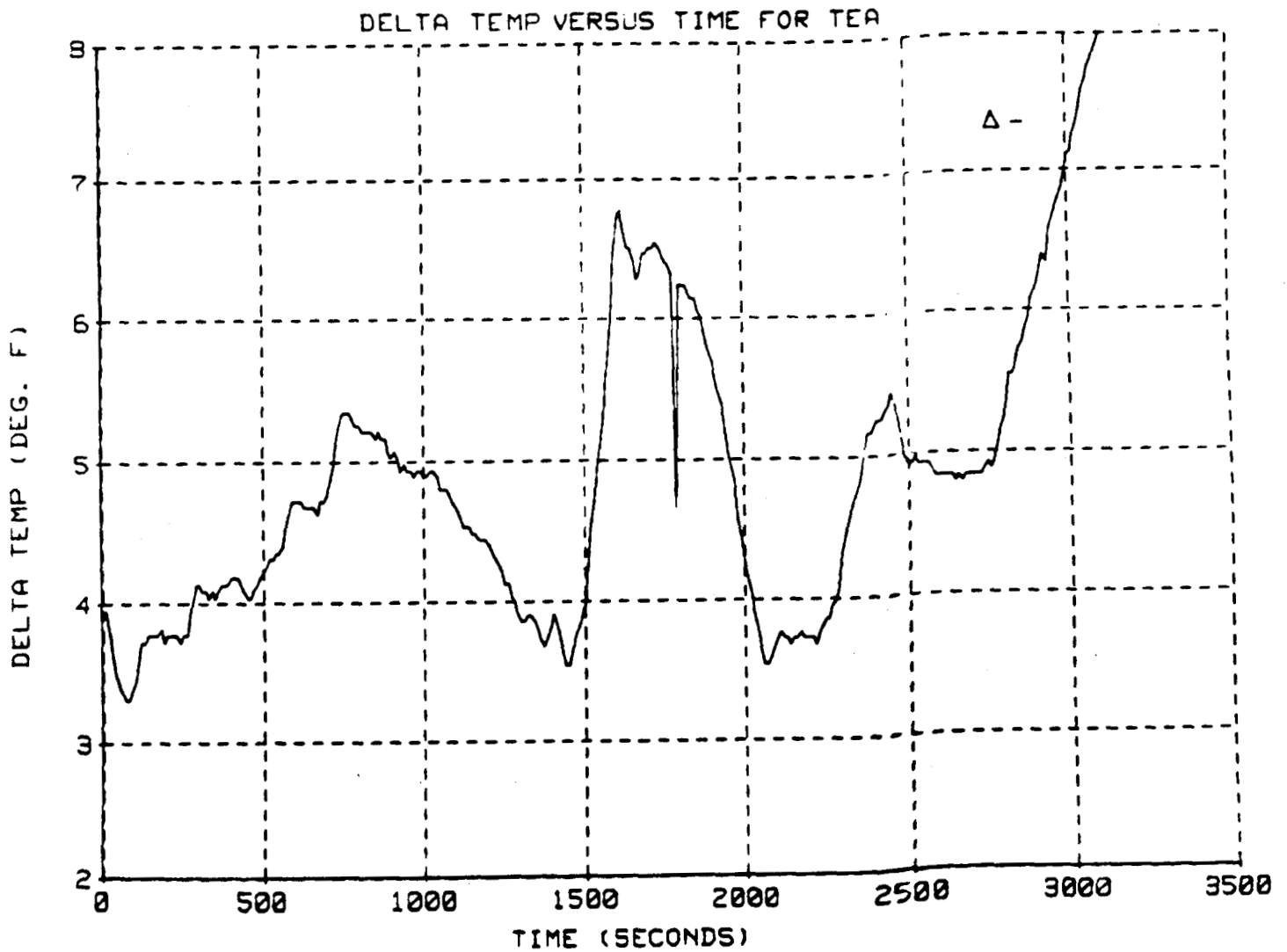


Fig. A-13 Delta Temperature vs Time for Triethylamine (TEA) (Run No. 4) (37.9% Triethylamine, 62.1% Water)

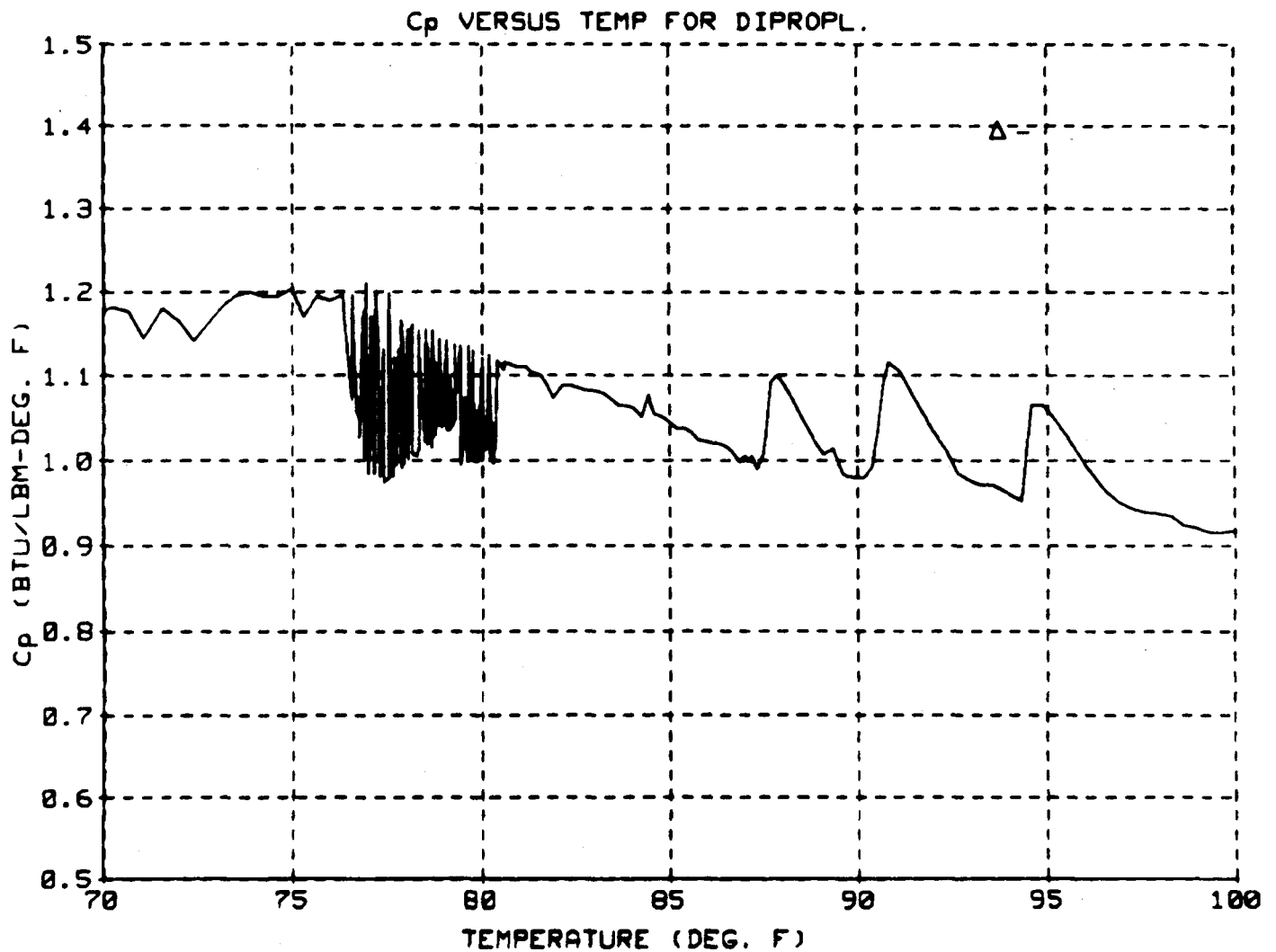


Fig. A-14 C_p vs Temperature for Diisopropylamine (Run No. 5)
(30% Diisopropylamine, 70% Water)

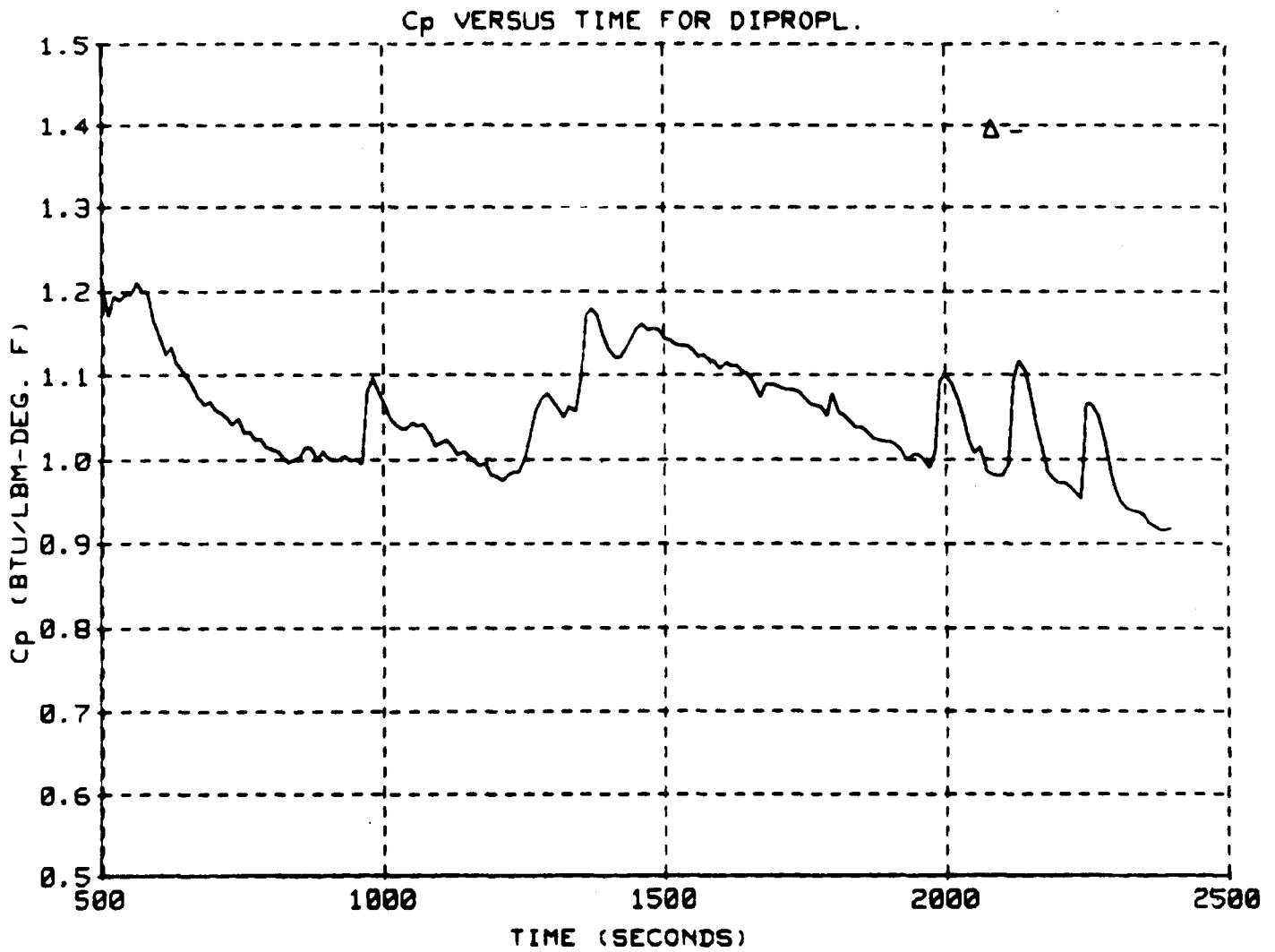


Fig. A-15 C_p vs Time for Diisopropylamine (Run No. 5)
(30% Diisopropylamine, 70% Water)

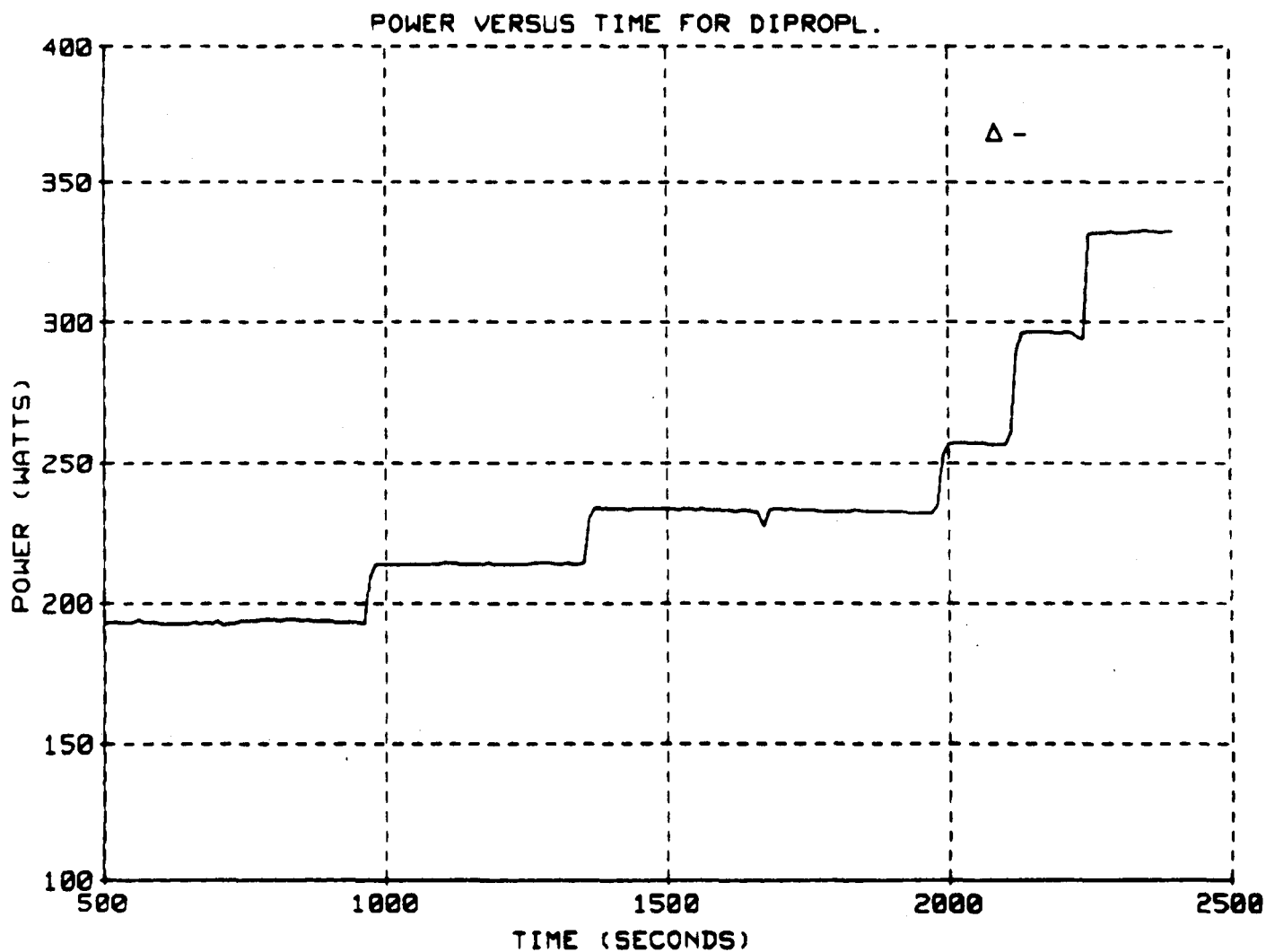


Fig. A-16 Power vs Time for Diisopropylamine (Run No. 5)
(30% Diisopropylamine, 70% Water)

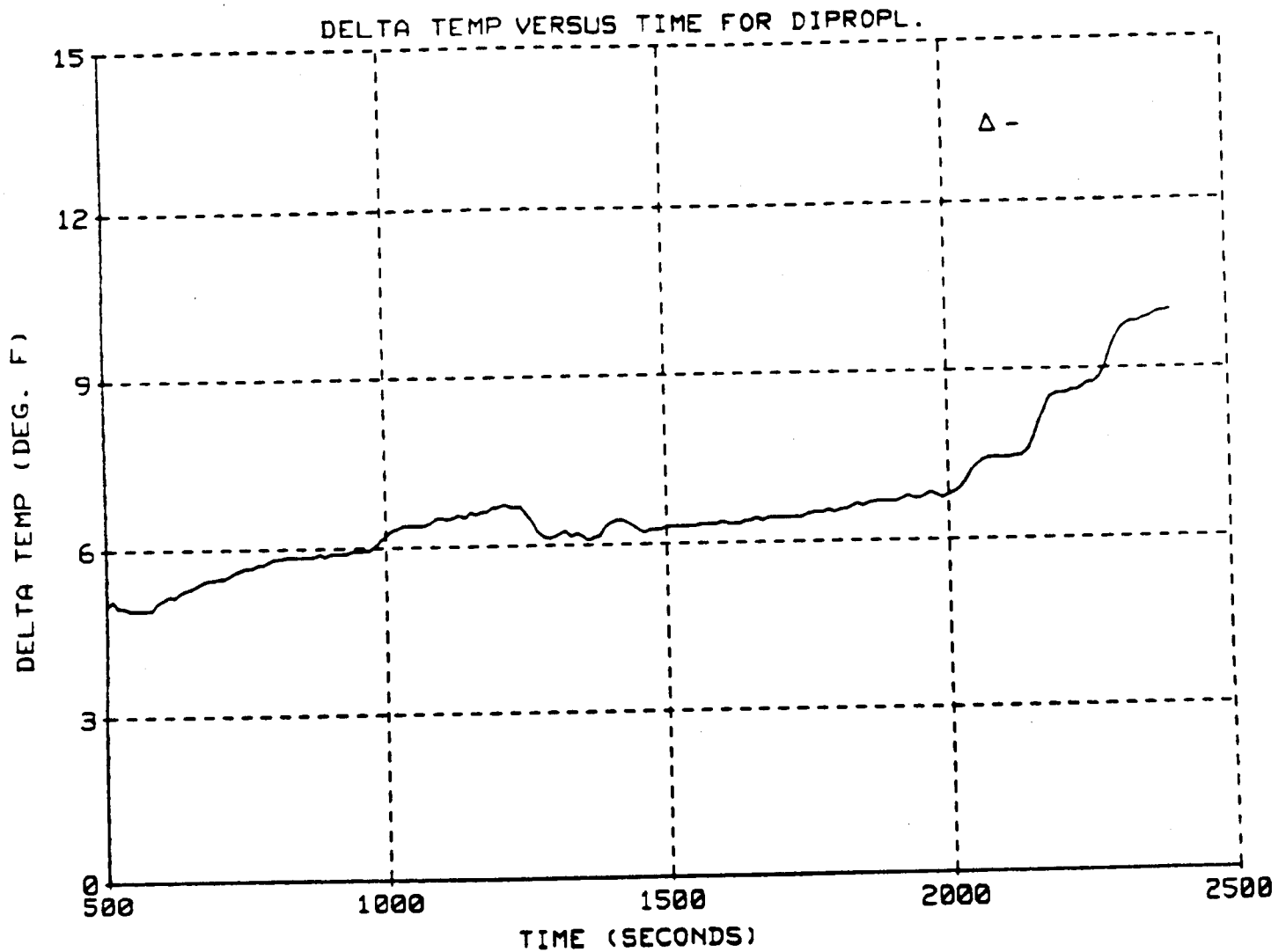


Fig. A-17 Delta Temperature vs Time for Diisopropylamine
(Run No. 5) (30% Diisopropylamine, 70% Water)

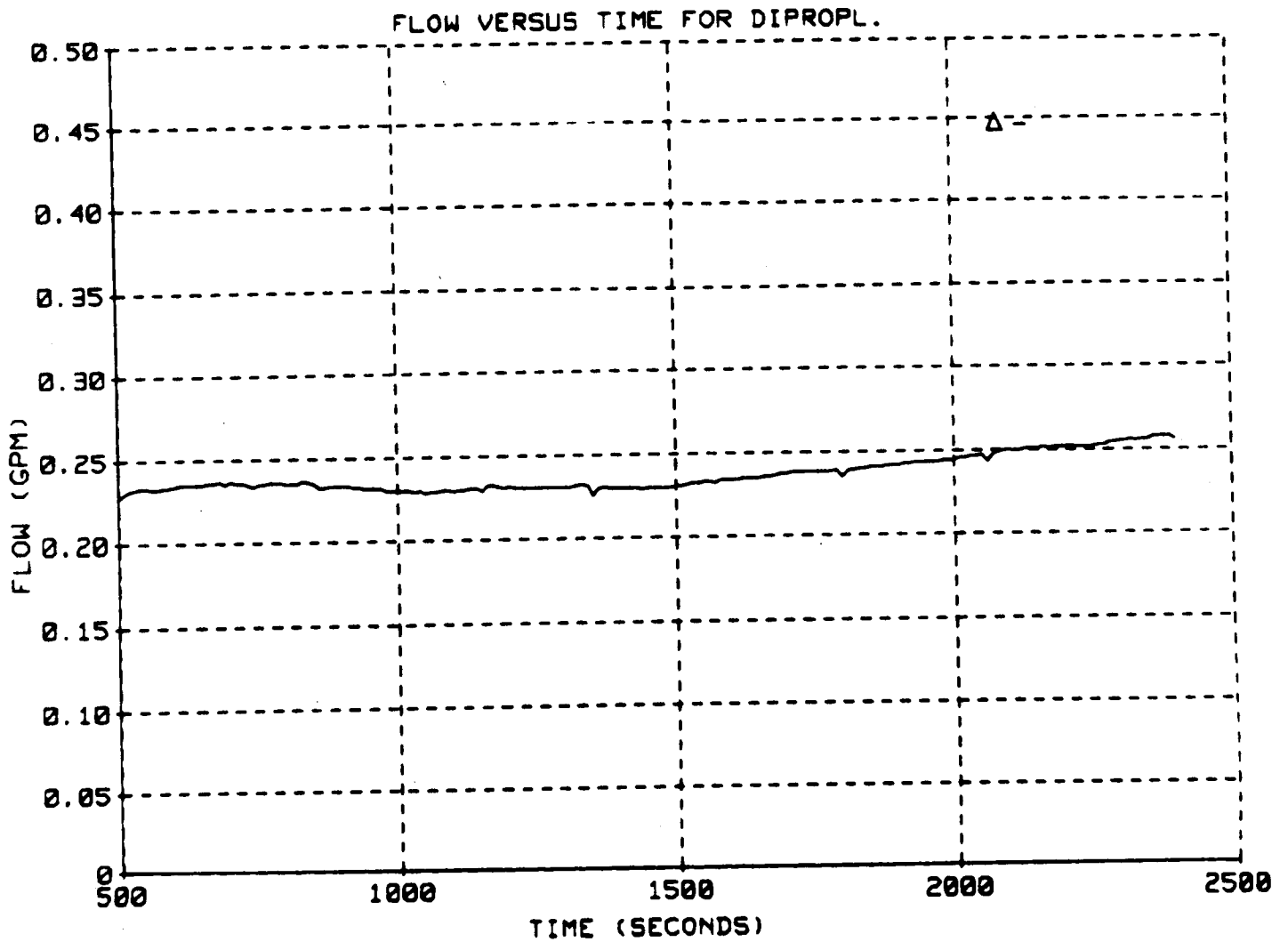


Fig. A-18 Flow Rate vs Time for Diisopropylamine (Run No. 5)
(30% Diisopropylamine, 70% Water)

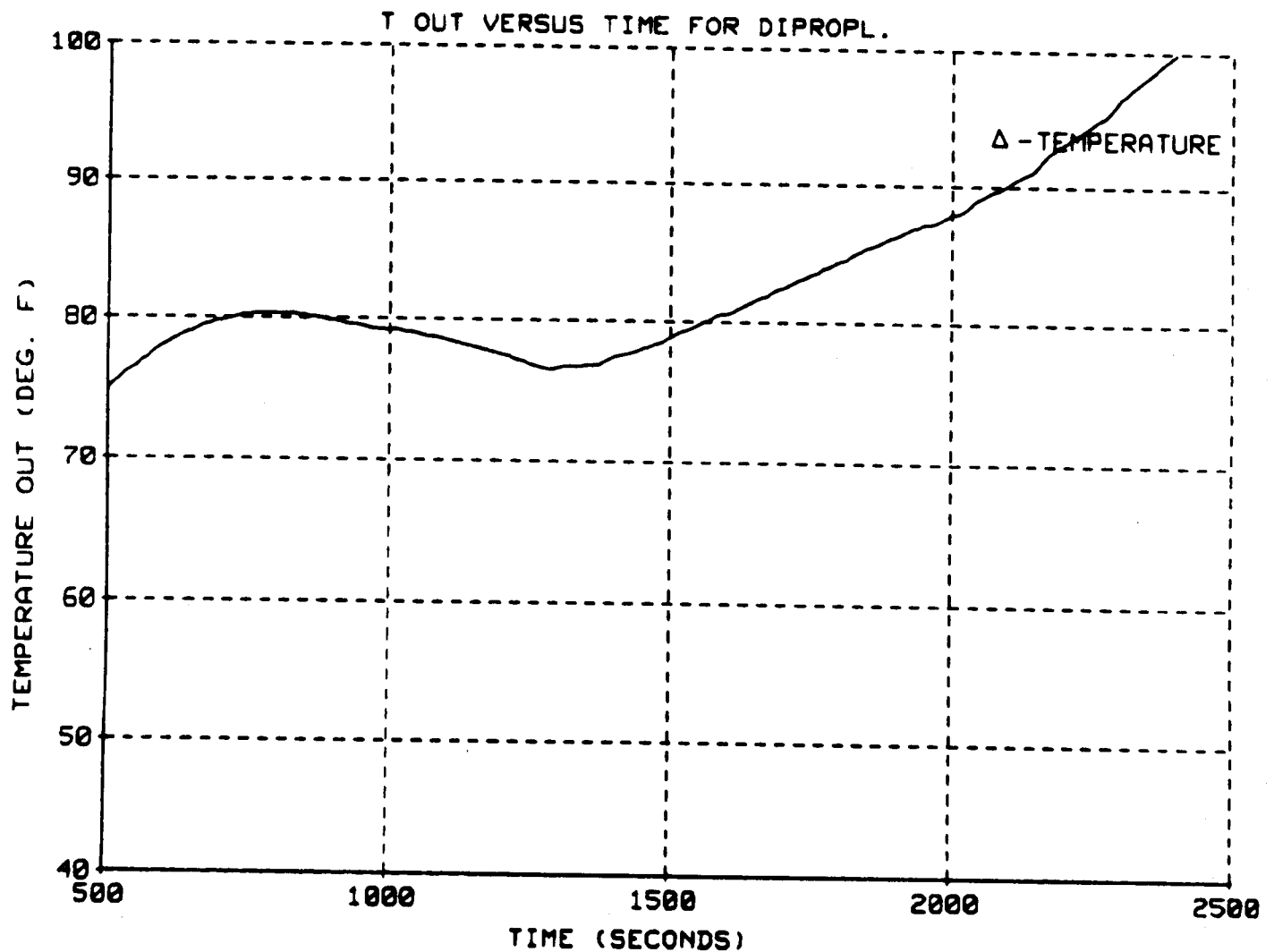


Fig. A-19 Outlet Temperature vs Time for Diisopropylamine
(Run No. 5) (30% Diisopropylamine, 70% Water)

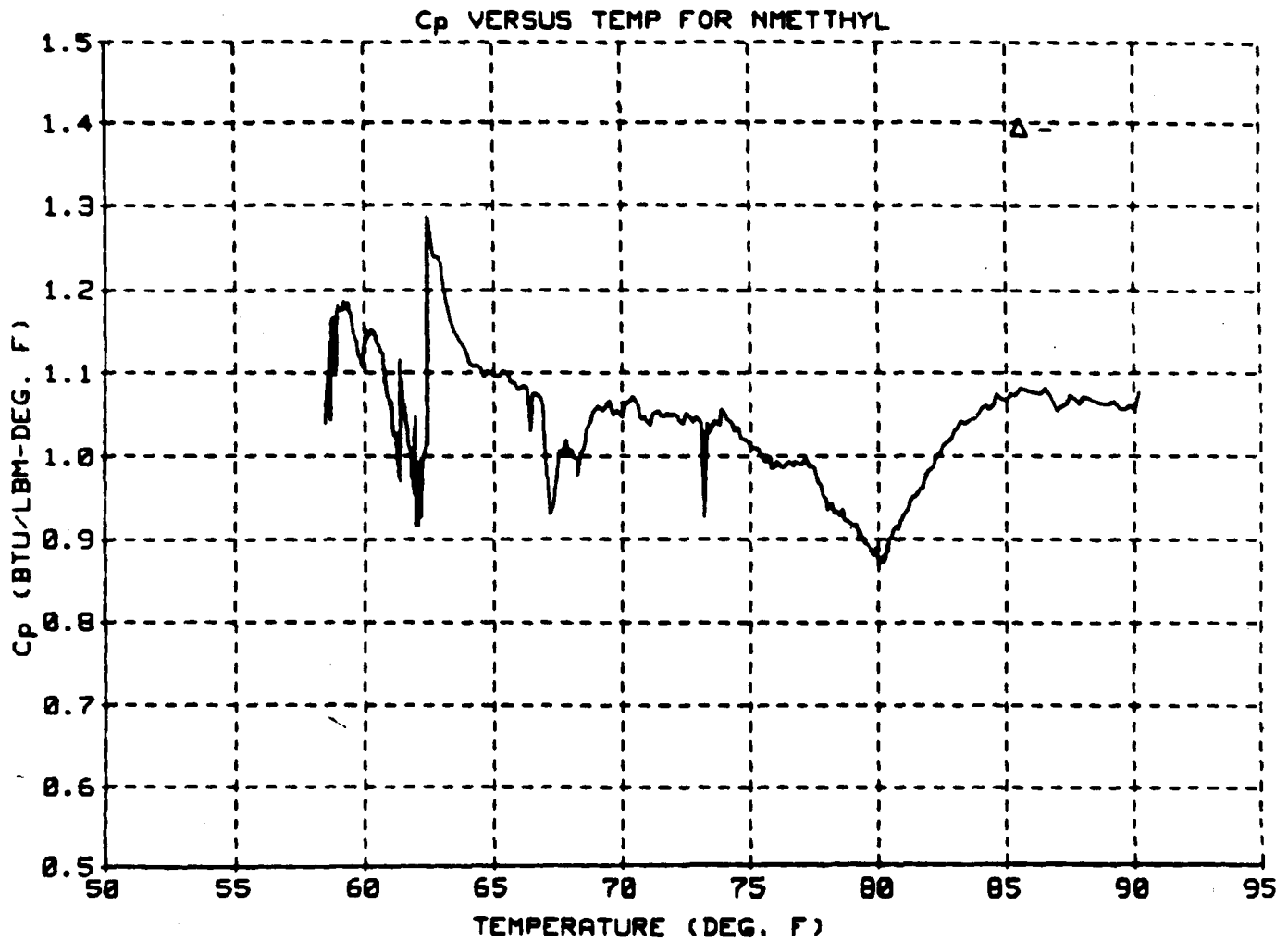


Fig. A-20 C_p vs Temperature for N-Methyl-Pyrrolidone (Run No. 6)
(73% N-Methyl-Pyrrolidone, 27% Water)

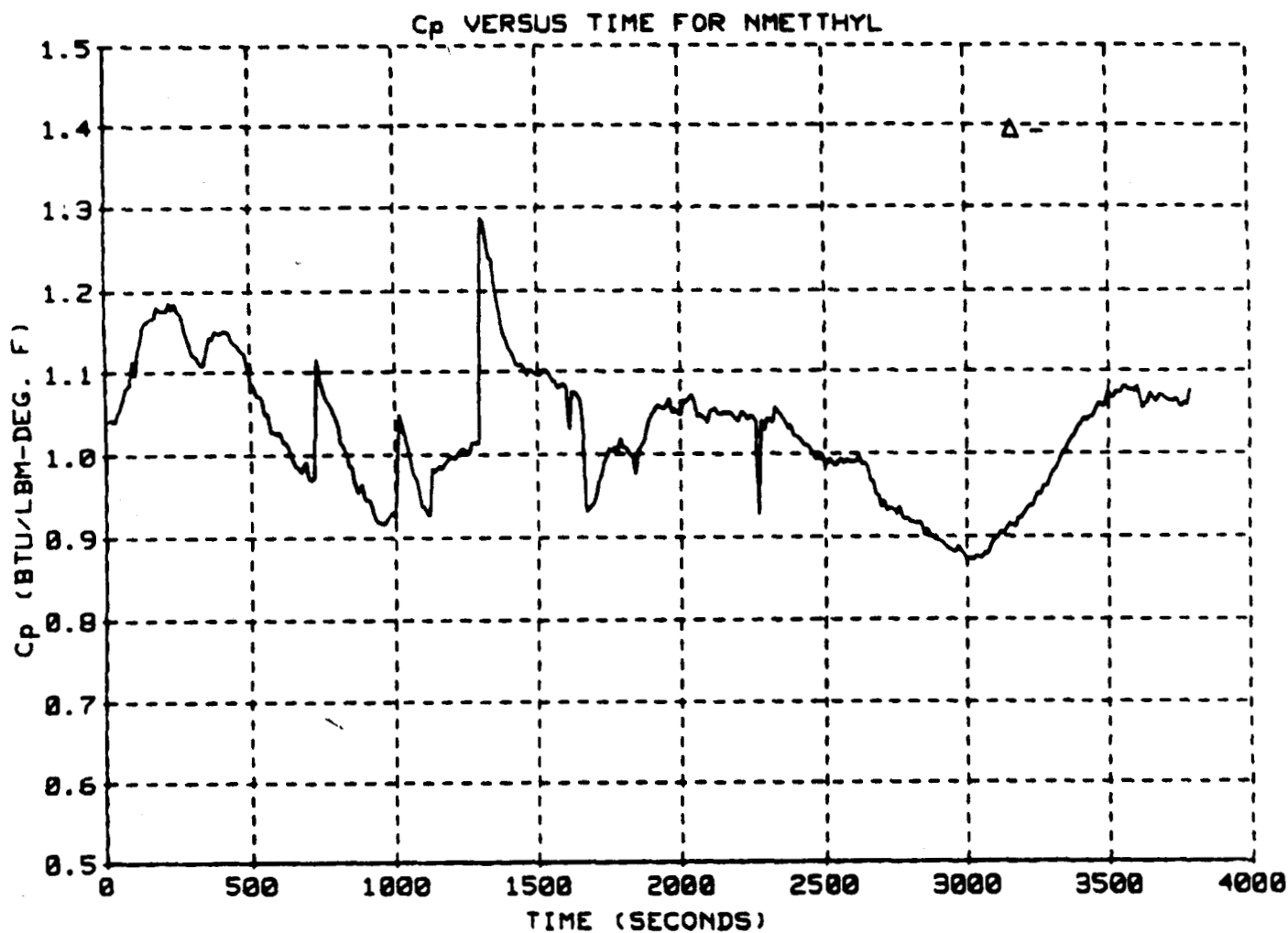


Fig. A-21 C_p vs Time for N-Methyl-Pyrrolidone (Run No. 6)
(73% N-Methyl-Pyrrolidone, 27% Water)

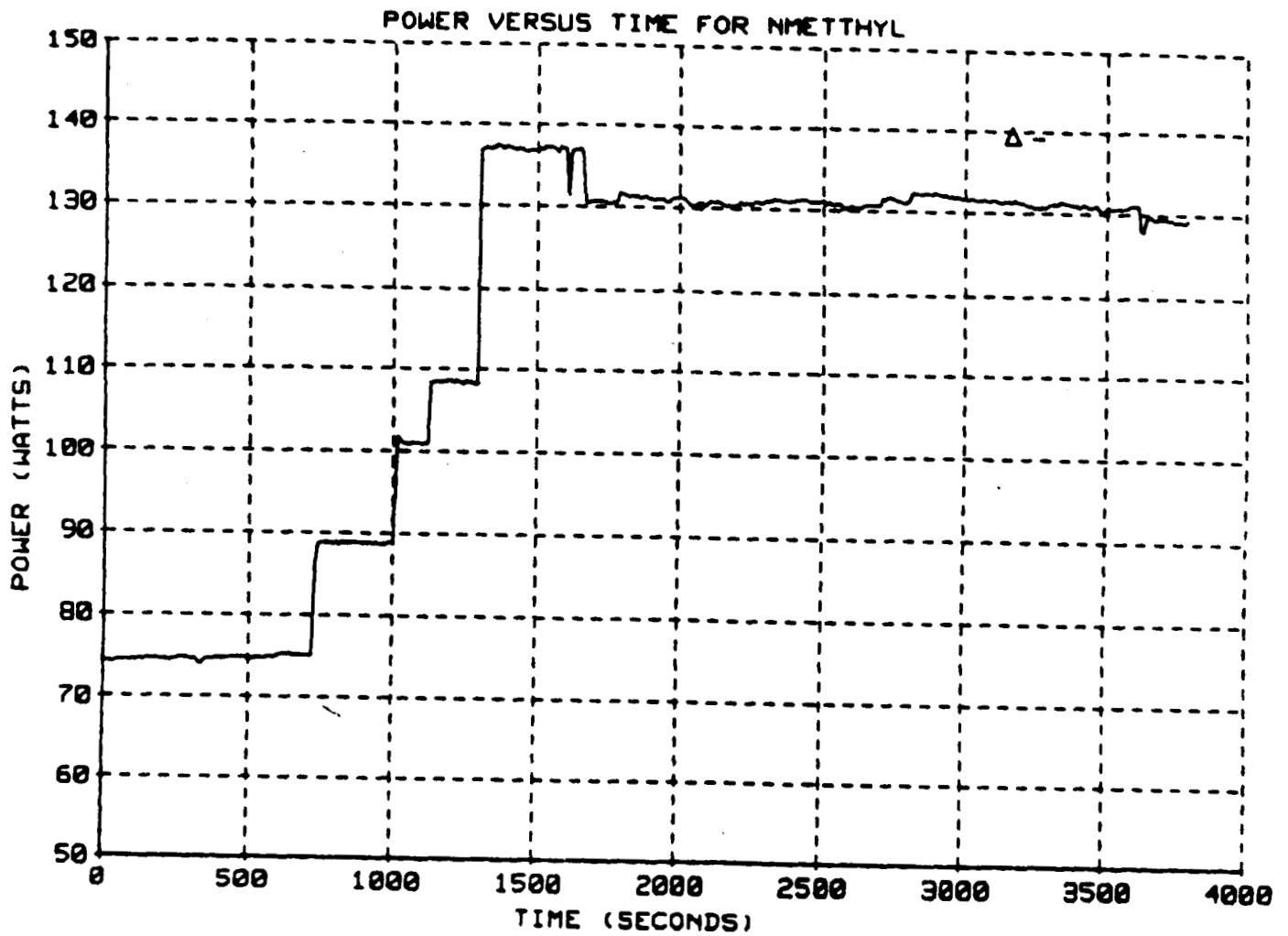


Fig. A-22 Power vs Time for N-Methyl-Pyrrolidone (Run No. 6)
(73% N-Methyl-Pyrrolidone, 27% Water)

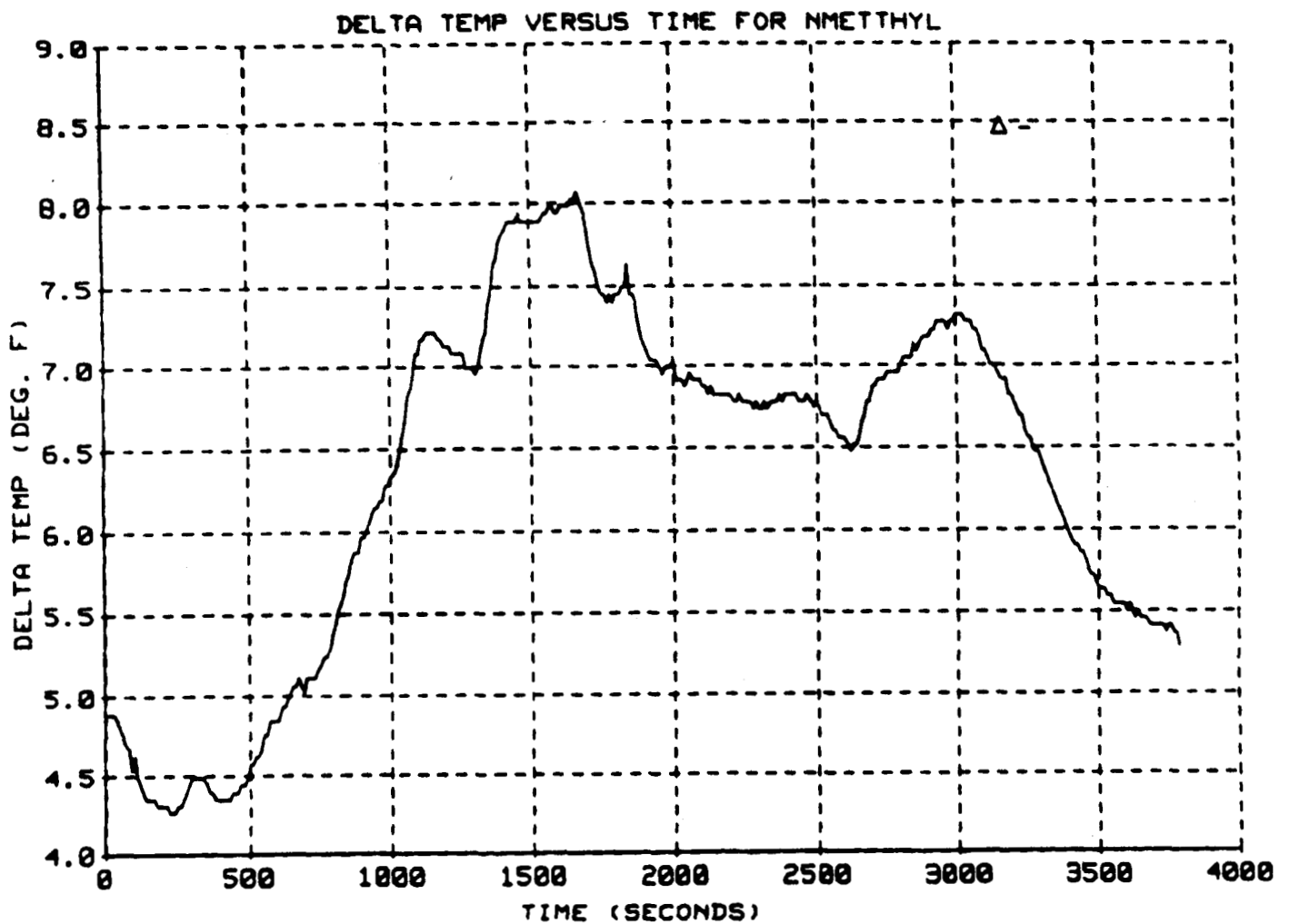


Fig. A-23 Delta Temperature vs Time for N-Methyl-Pyrrolidone
(Run No. 6) (73% N-Methyl-Pyrrolidone, 27% Water)

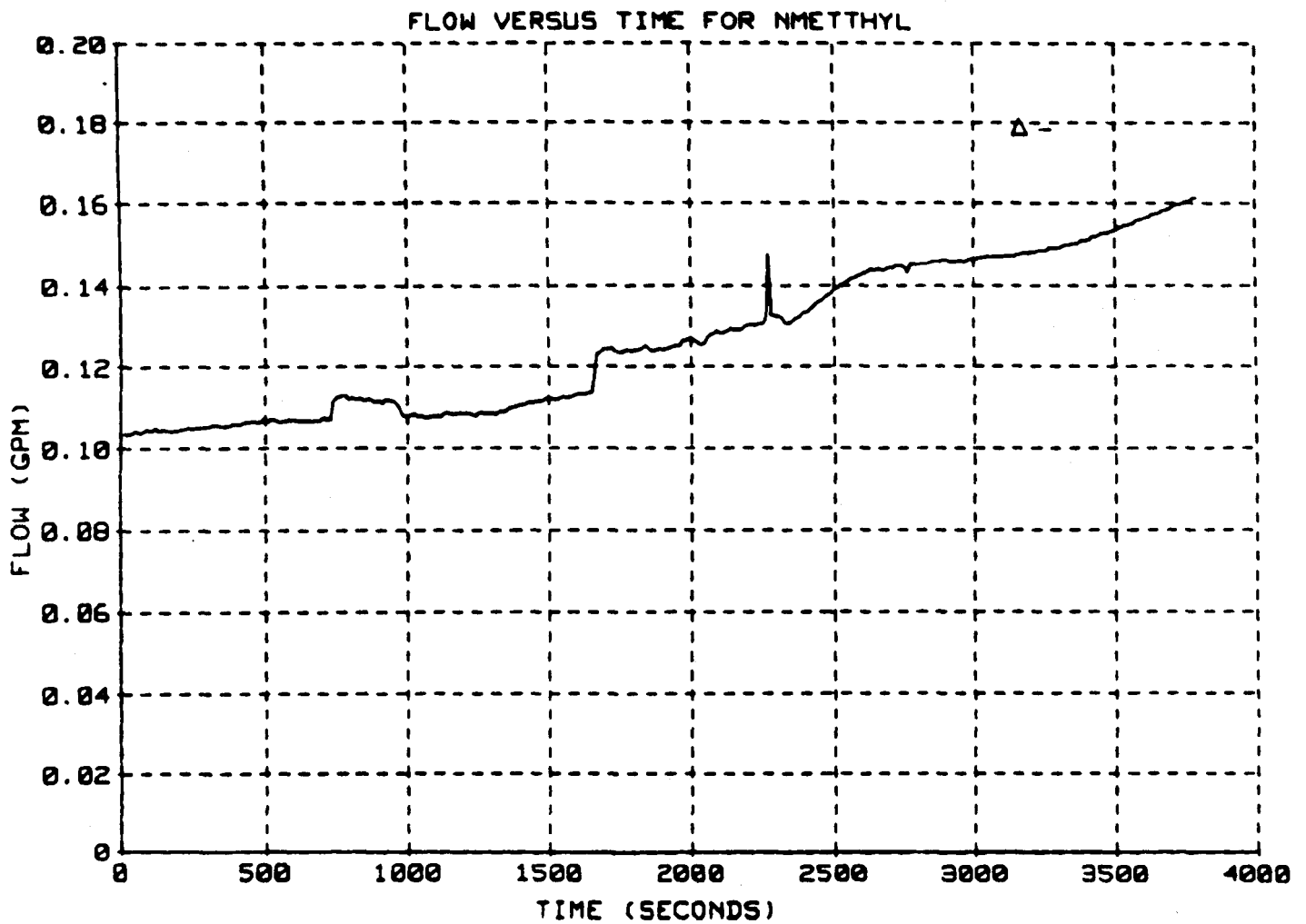


Fig. A-24 Flow vs Time for N-Methyl-Pyrrolidone (Run No. 6)
(73% N-Methyl-Pyrrolidone, 27% Water)

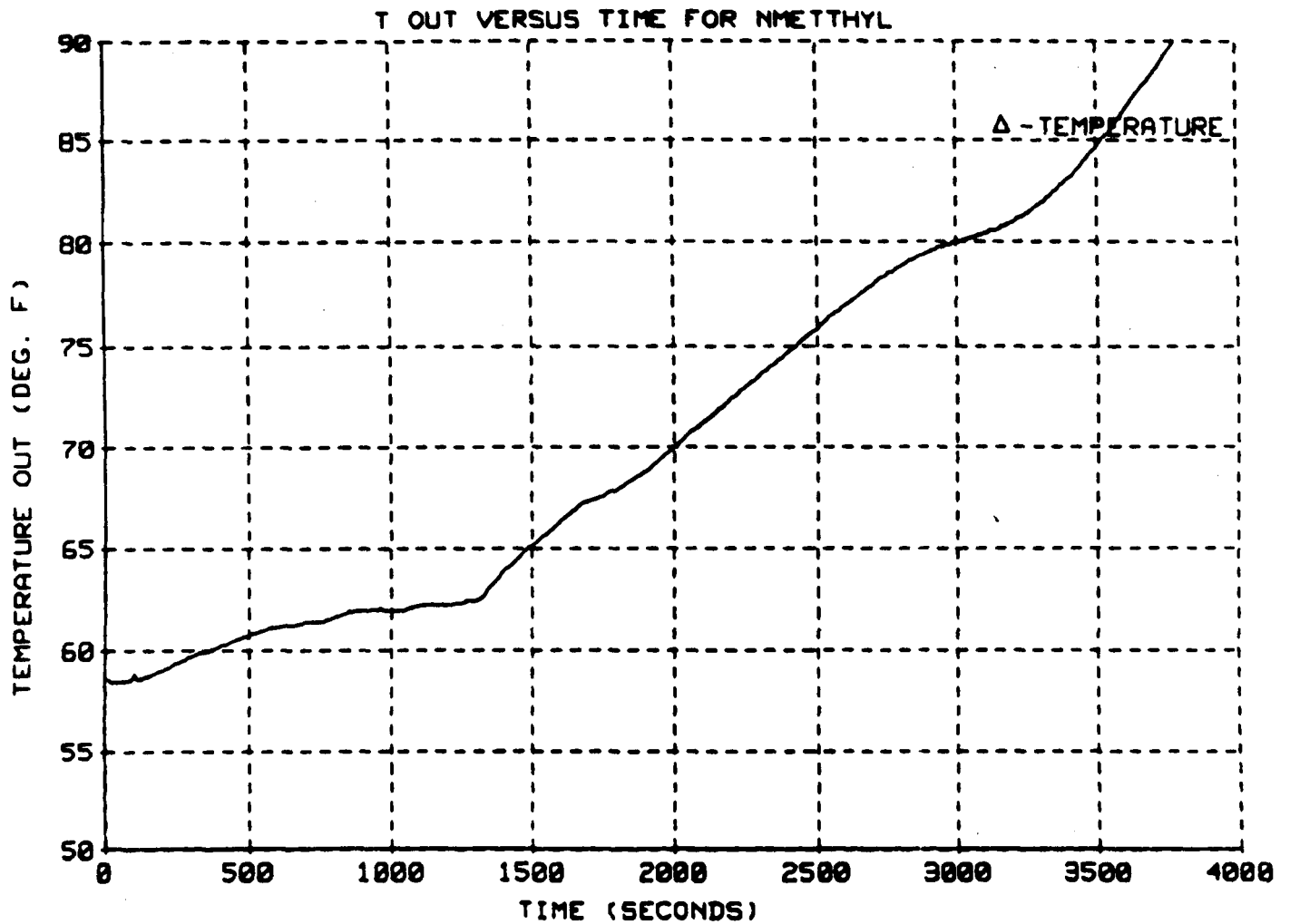


Fig. A-25 Outlet Temperature vs Time for N-Methyl-Pyrrolidone
(Run No. 6) (73% N-Methyl-Pyrrolidone, 27% Water)

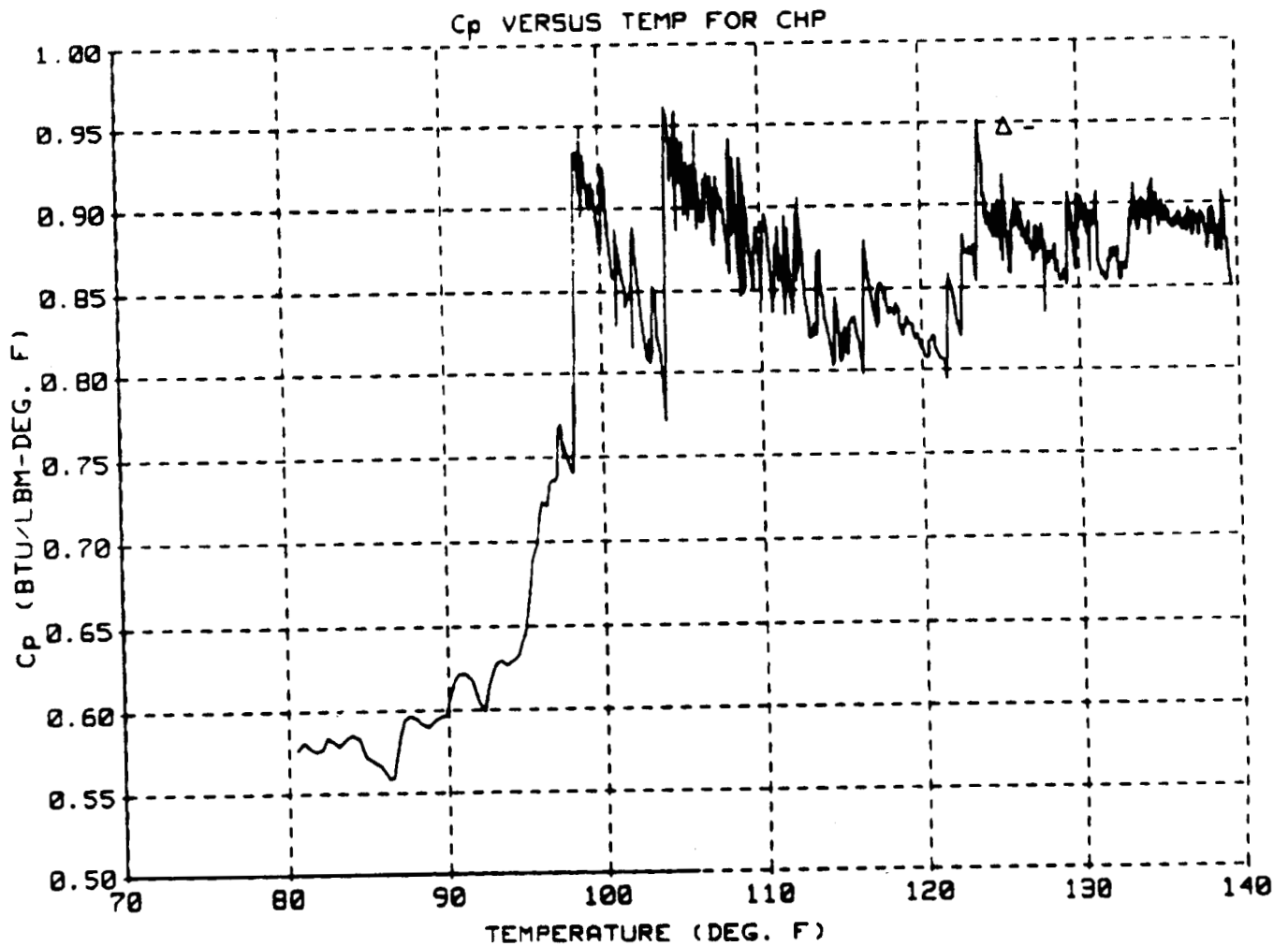


Fig. A-26 C_p vs Temperature for N-Cyclohexyl-2-Pyrrolidone (CHP)
(Run No. 9) (30% N-Cyclohexyl-2-Pyrrolidone, 70% Water)

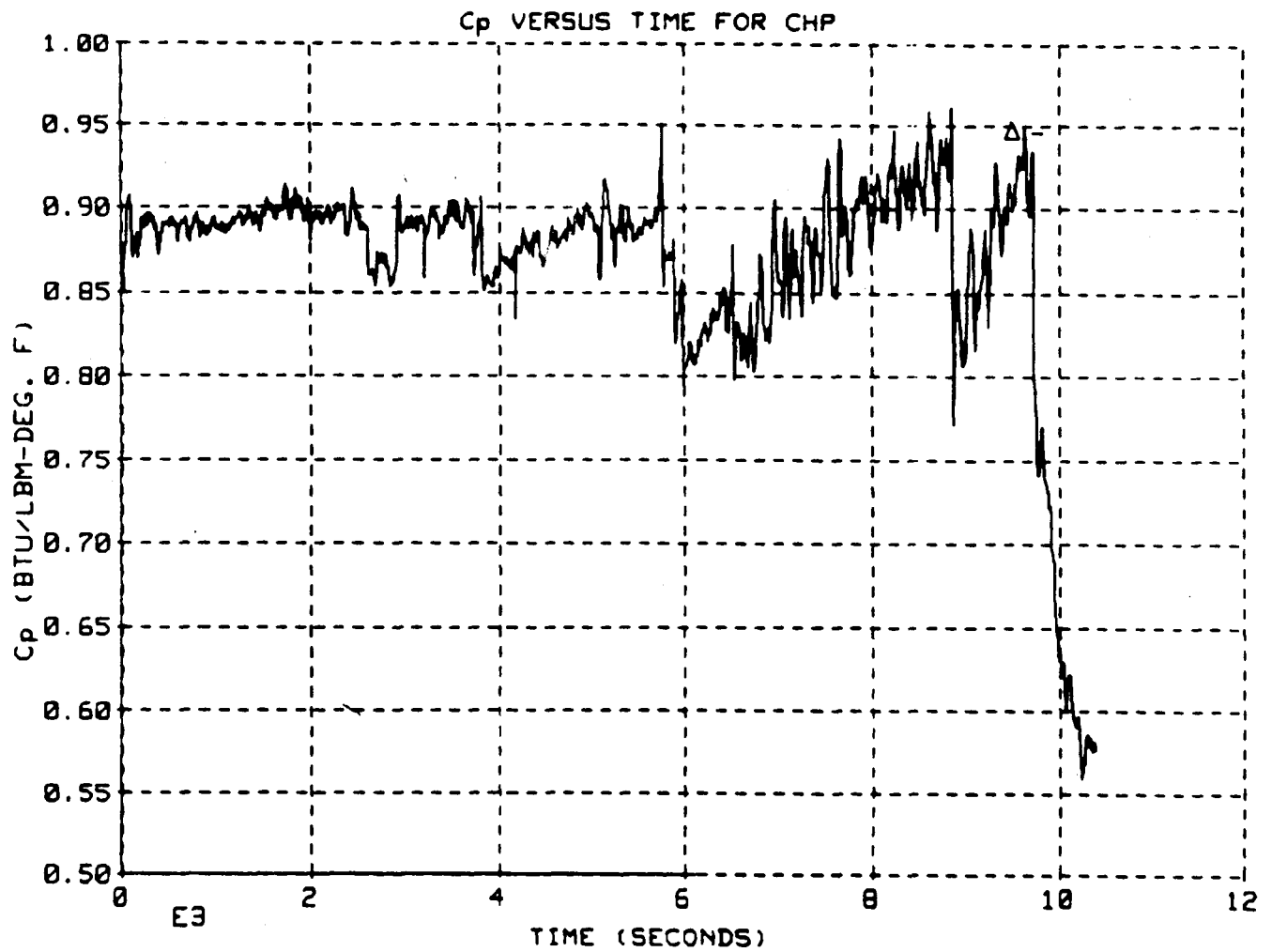


Fig. A-27 C_p vs Time for N-Cyclohexyl-2-Pyrrolidone (CHP) (Run No. 9)
(30% N-Cyclohexyl-2-Pyrrolidone, 70% Water)

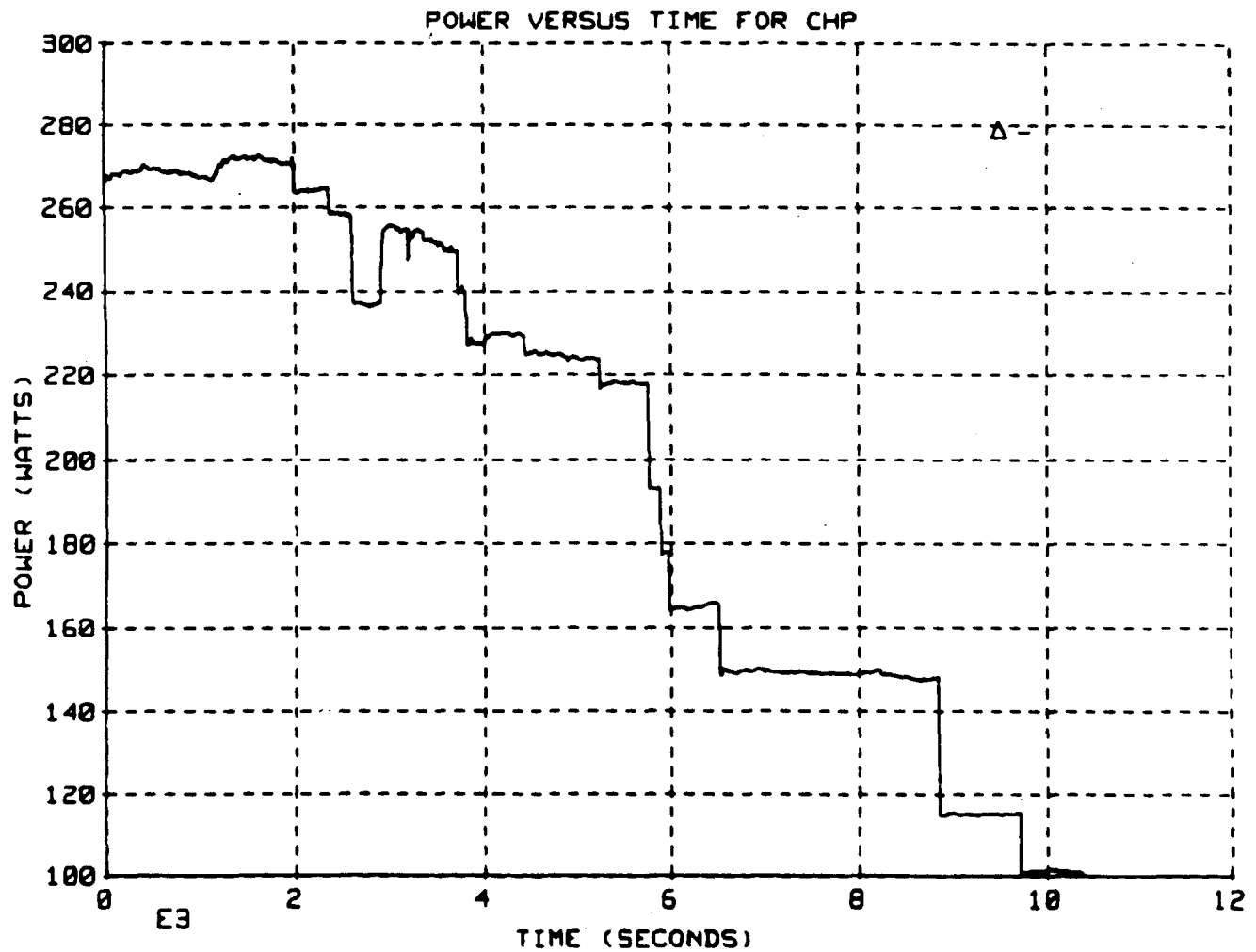


Fig. A-28 Power vs Time for N-Cyclohexyl-2-Pyrrolidone (CHP) (Run No. 9)
(30% N-Cyclohexyl-2-Pyrrolidone, 70% Water)

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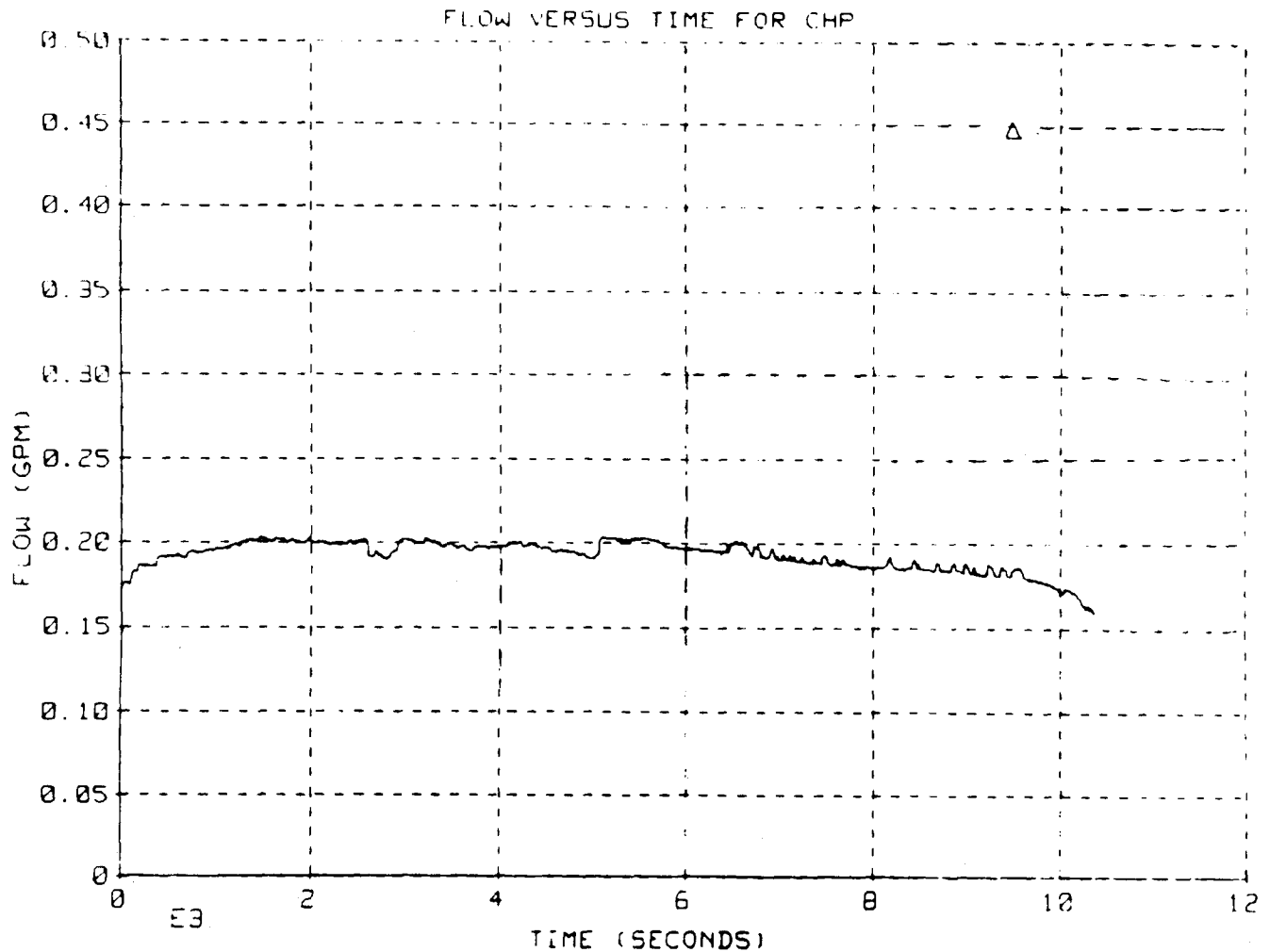


Fig. A-29 Flow vs Time for N-Cyclohexyl-2-Pyrrolidone (CHP) (Run No. 9)
(30% N-Cyclohexyl-2-Pyrrolidone, 70% Water)

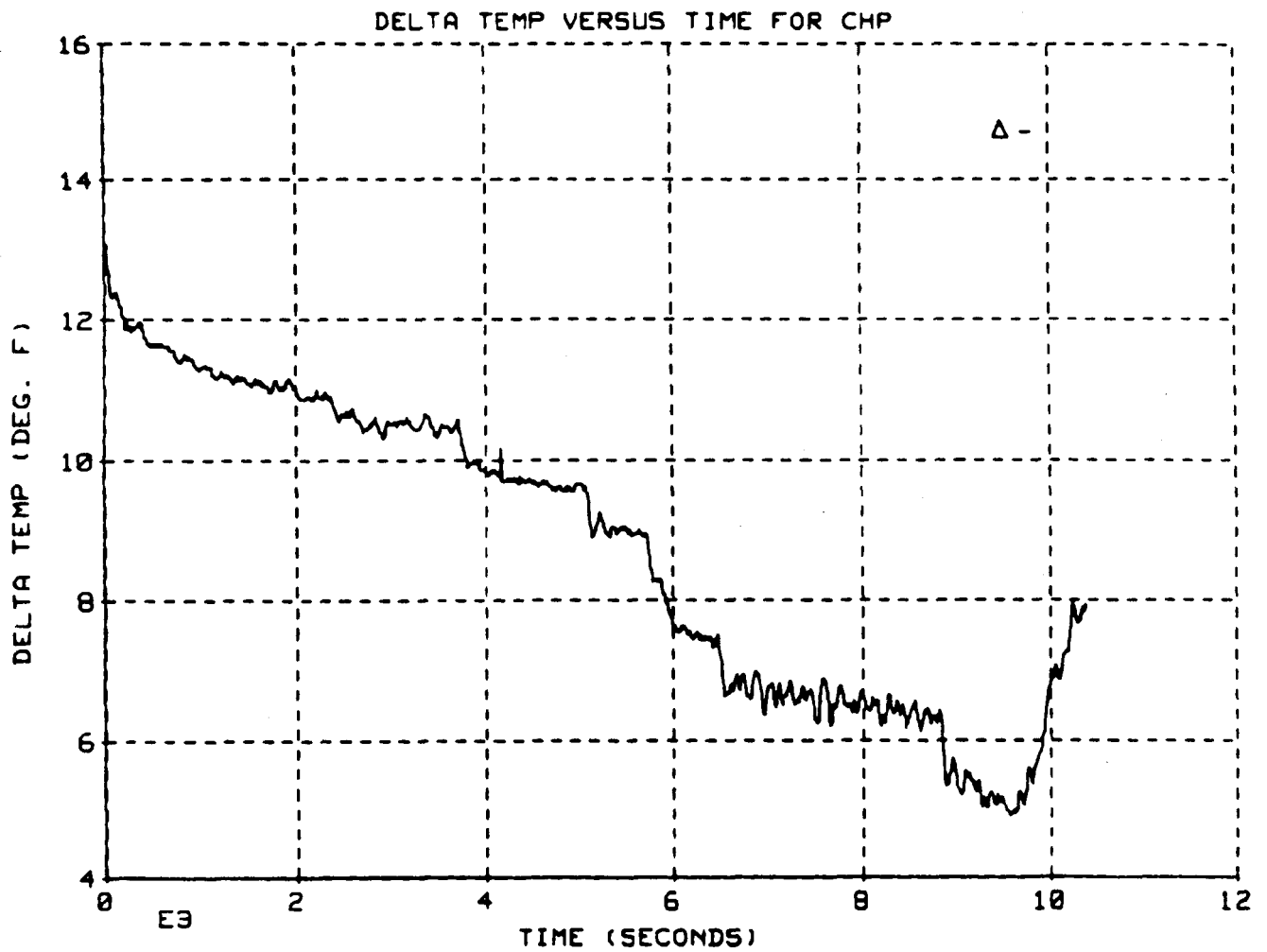


Fig. A-30 Delta Temperature vs Time for N-Cyclohexyl-2-Pyrrolidone (CHP)
(Run No. 9) (30% N-Cyclohexyl-2-Pyrrolidone, 70% Water)



Fig. A-31 Outlet Temperature vs Time for N-Cyclohexyl-2-Pyrrolidone (CHP)
(Run No. 9) (30% N-Cyclohexyl-2-Pyrrolidone, 70% Water)

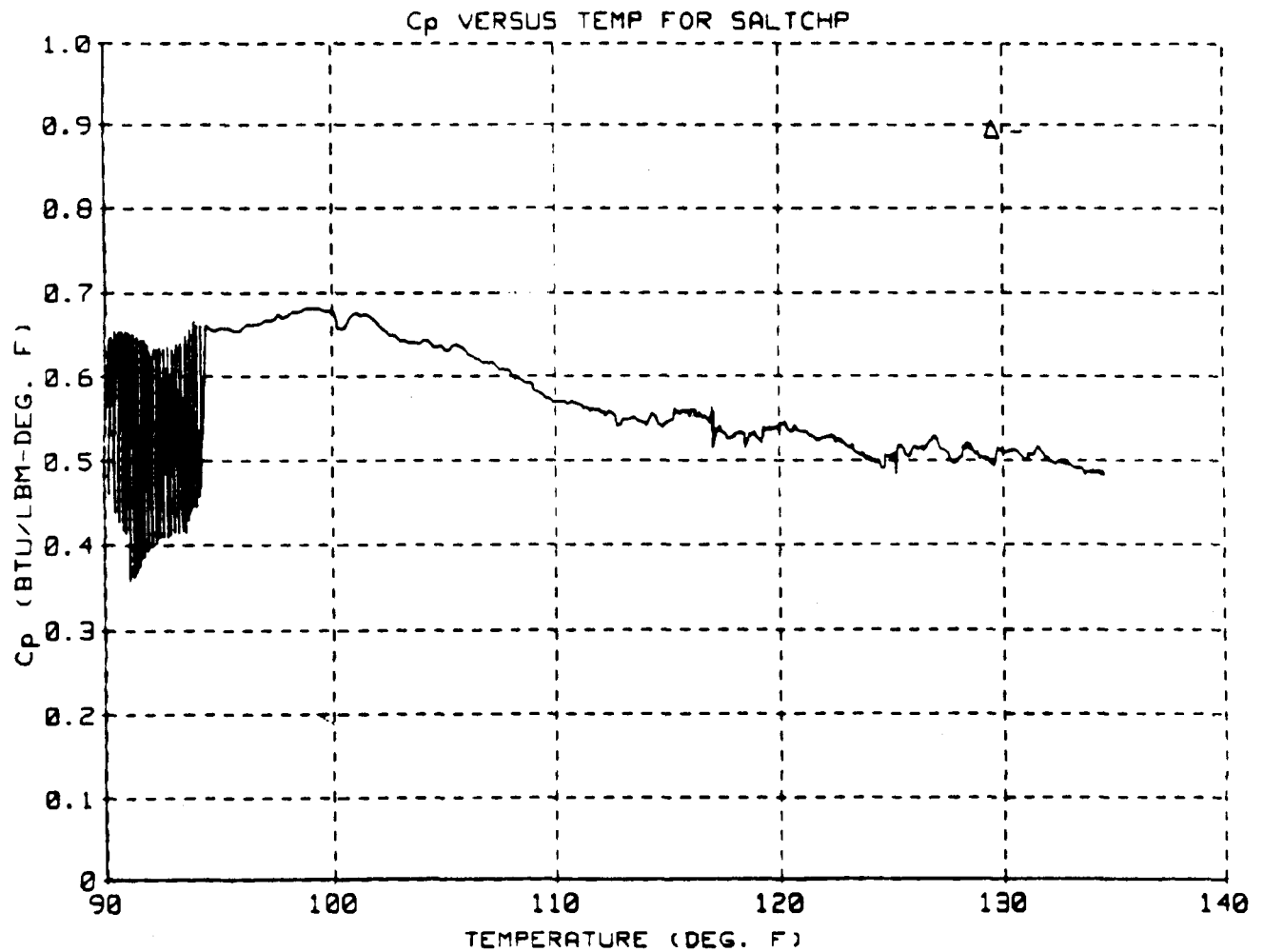


Fig. A-32 C_p vs Temperature for CHP and NaCl and H₂O (Run No. 10)
(30% CHP, 4% Salt, 66% Water)

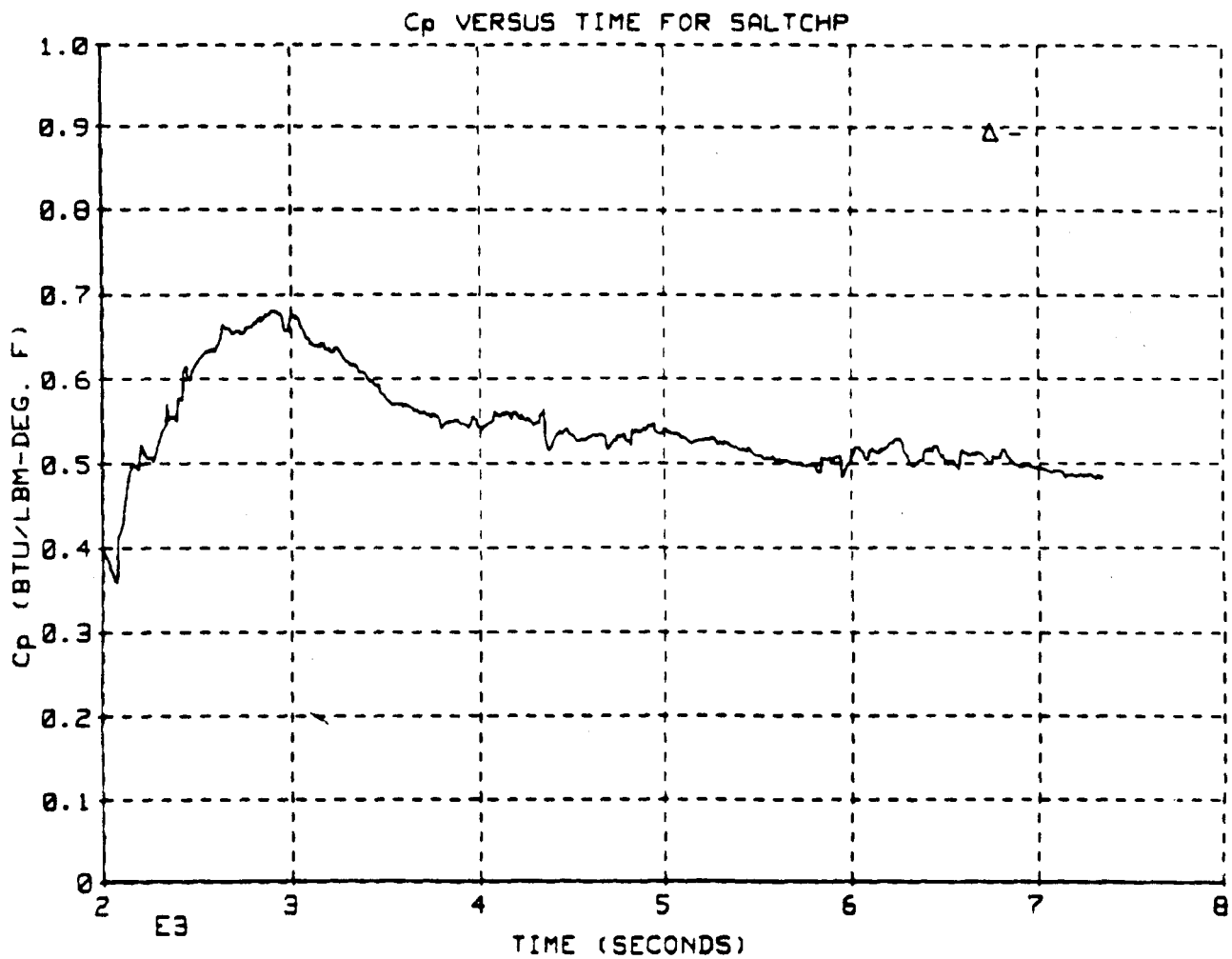


Fig. A-33 C_p vs Time for CHP and NaCl and H₂O (Run No. 10)
(30% CHP, 4% Salt, 66% Water)

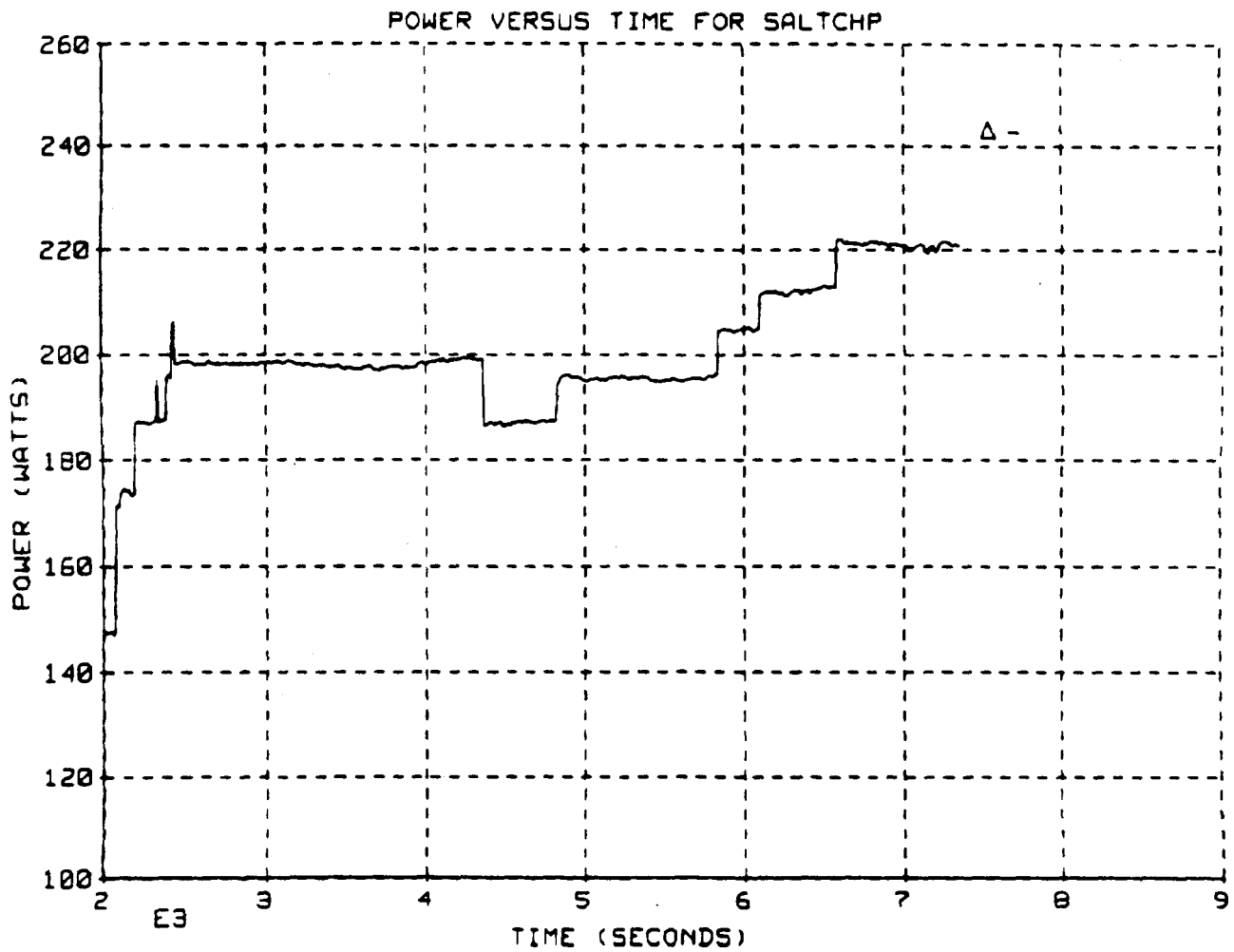


Fig. A-34 Power vs Time for CHP and NaCl and H₂O (Run No. 10)
(30% CHP, 4% Salt, 66% Water)

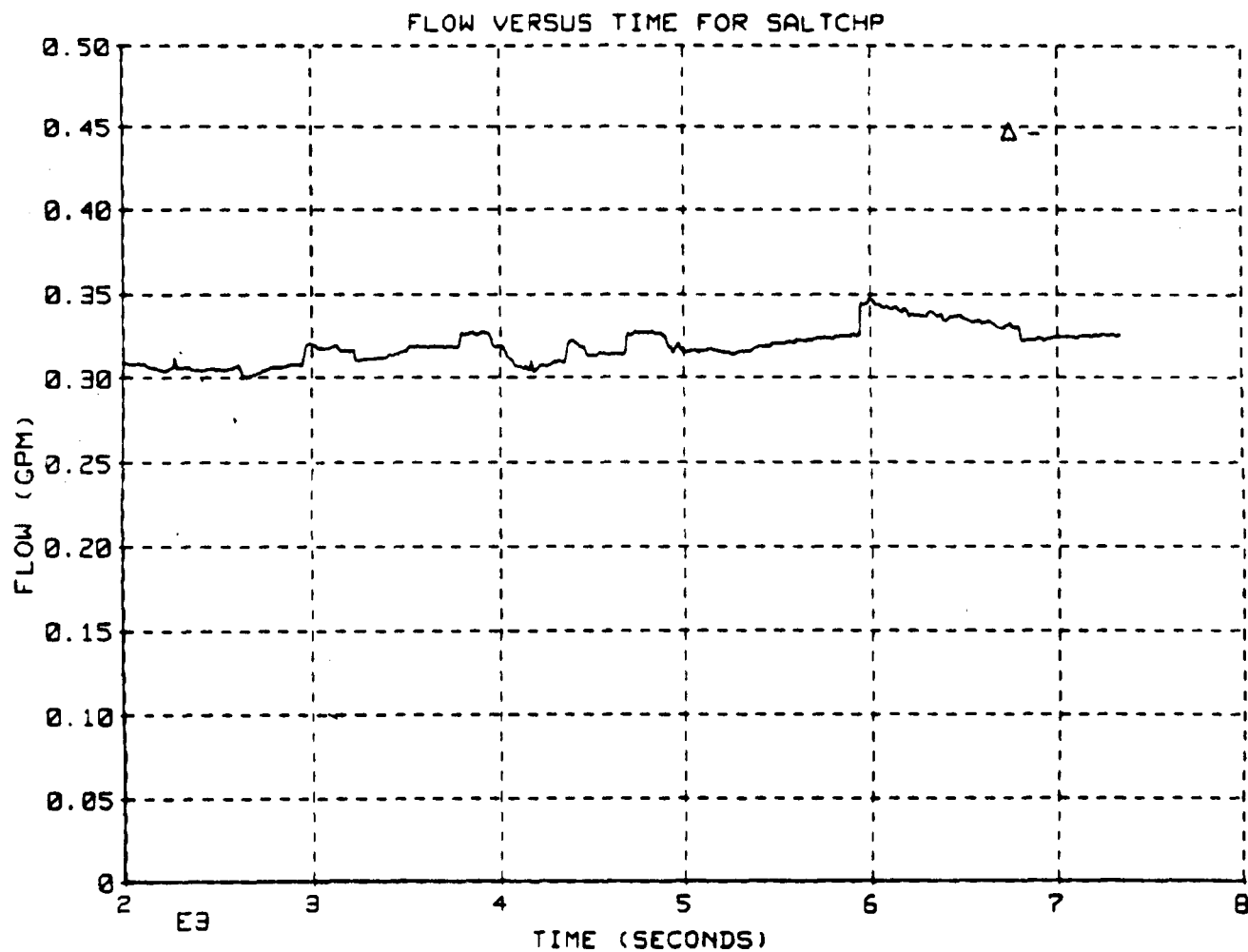


Fig. A-35 Flow vs Time for CHP and NaCl and H₂O (Run No. 10)
(30% CHP, 4% Salt, 66% Water)

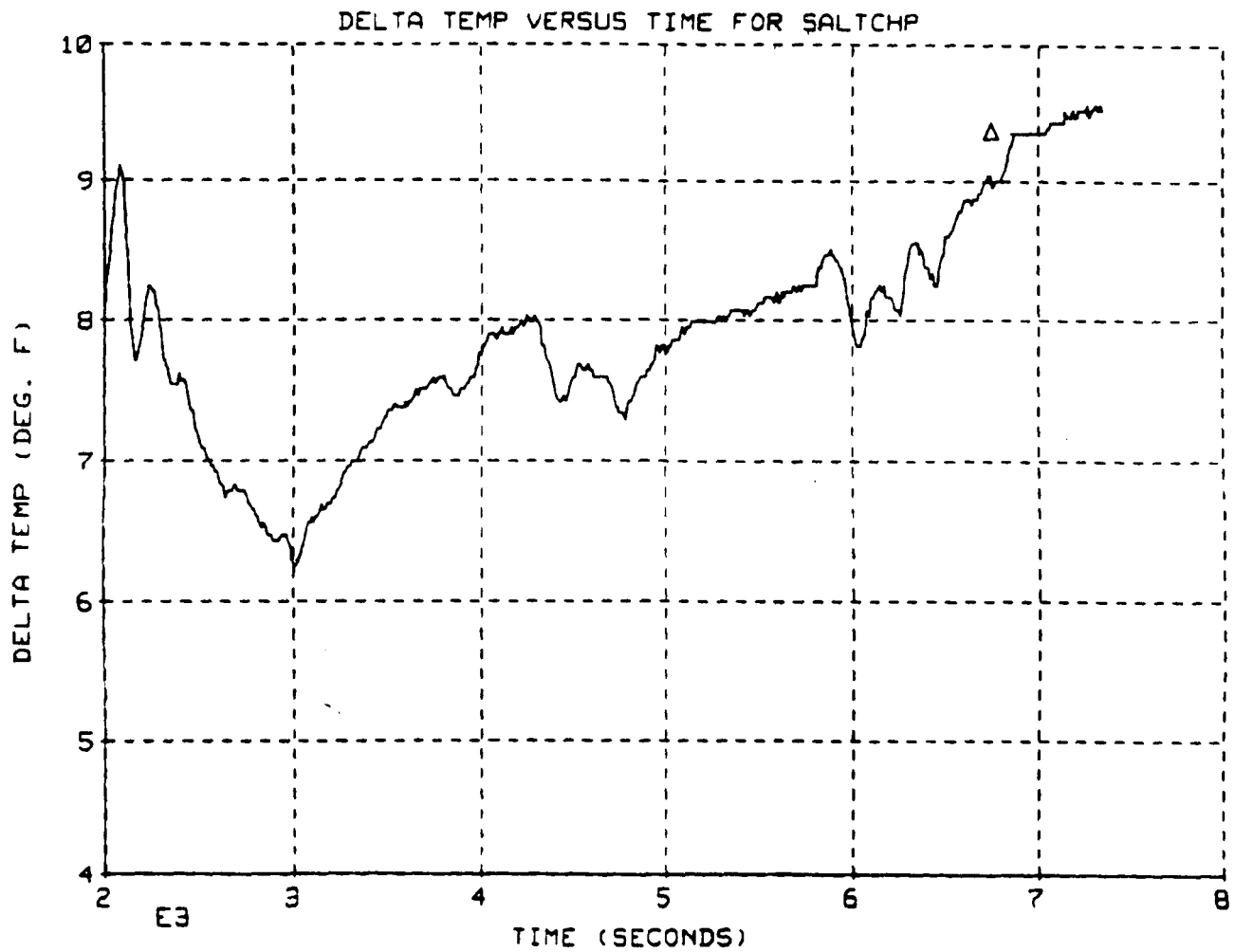


Fig. A-36 Delta Temperature vs Time for CHP and NaCl and H₂O
(Run No. 10) (30% CHP, 4% Salt, 66% Water)

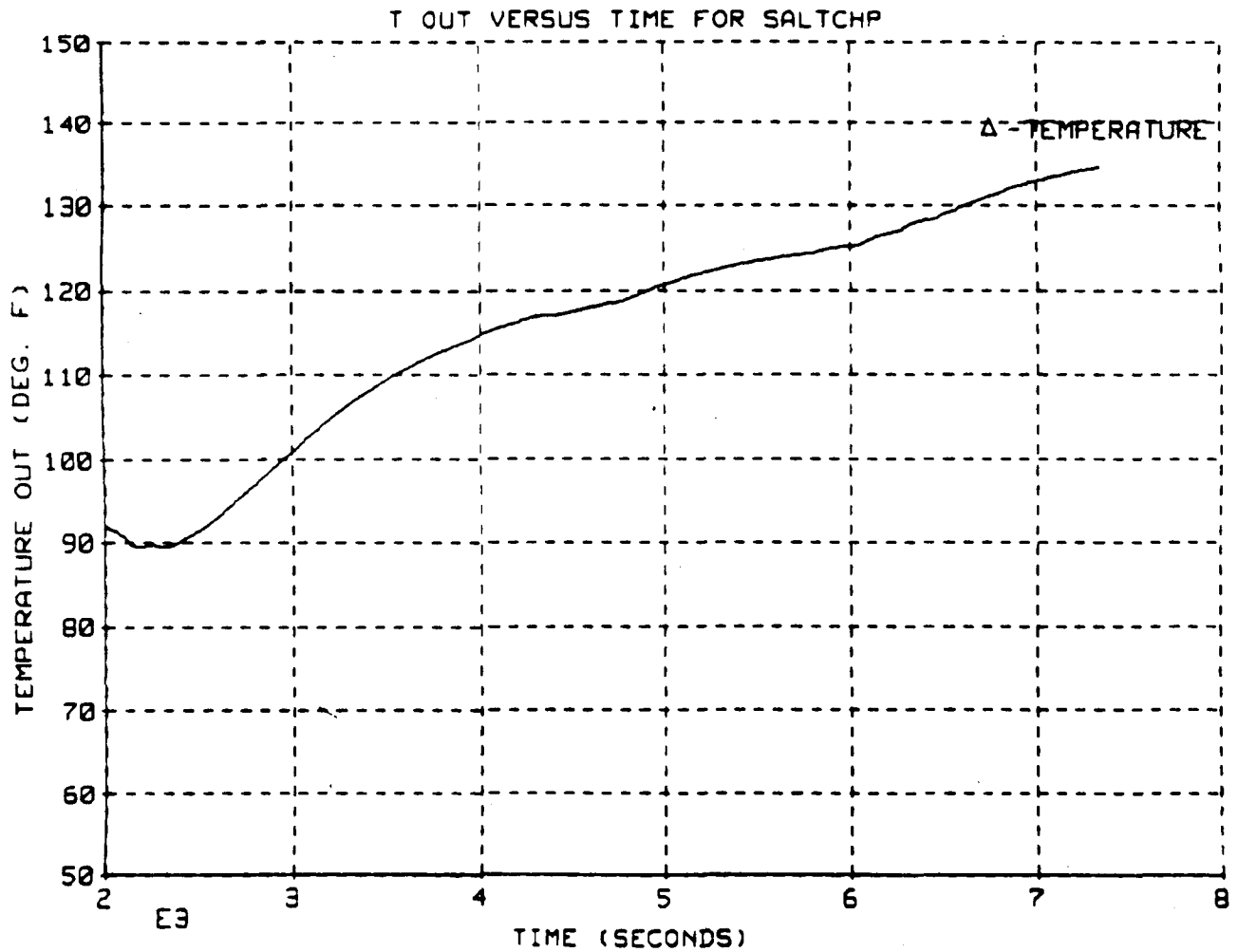


Fig. A-37 Outlet Temperature vs Time for CHP and NaCl and H₂O
(Run No. 10) (30% CHP, 4% Salt, 66% Water)

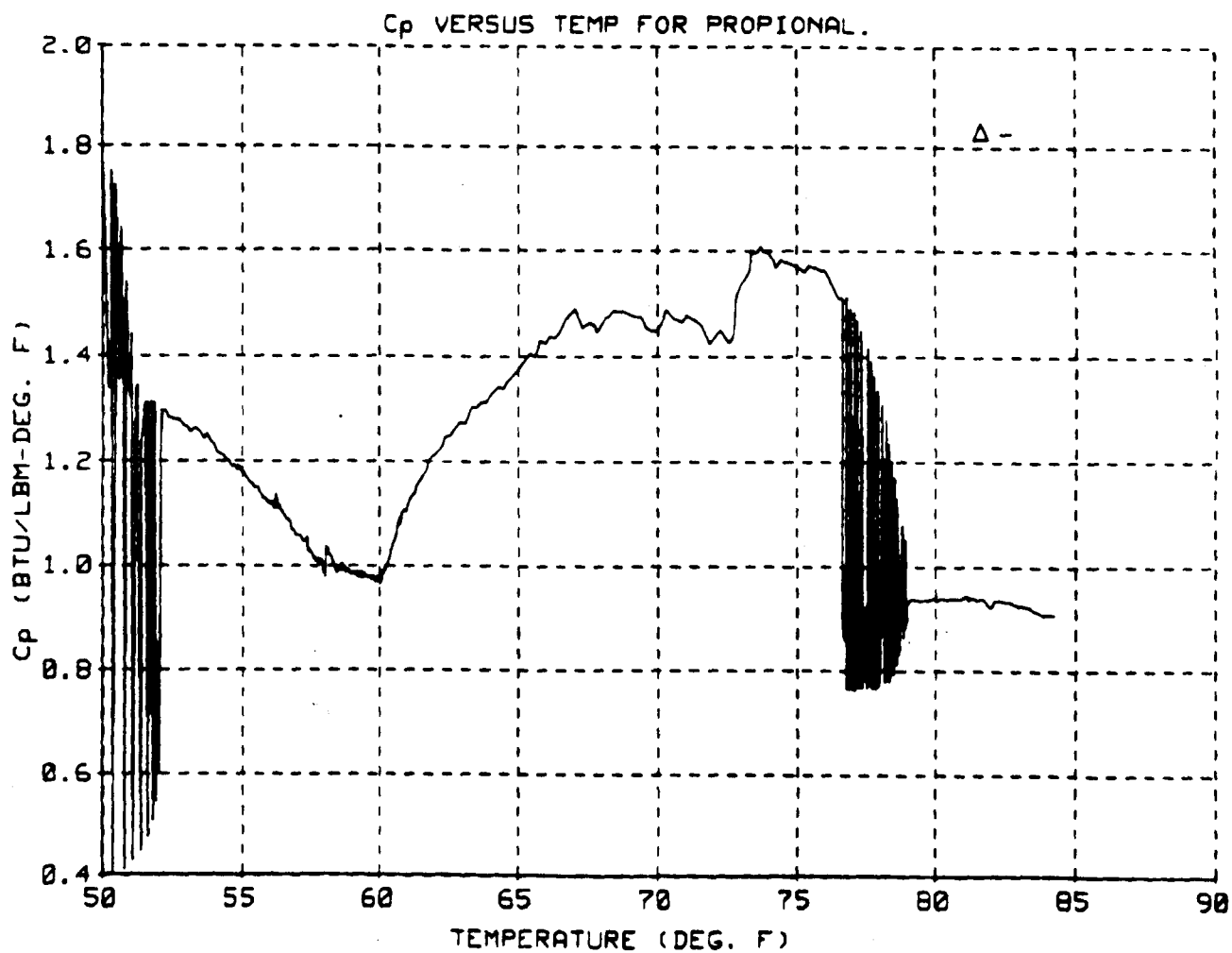


Fig. A-38 C_p vs Temperature for Propionaldehyde and H₂O
(Run No. 11a) (67.5% Propionaldehyde, 32.5% Water)

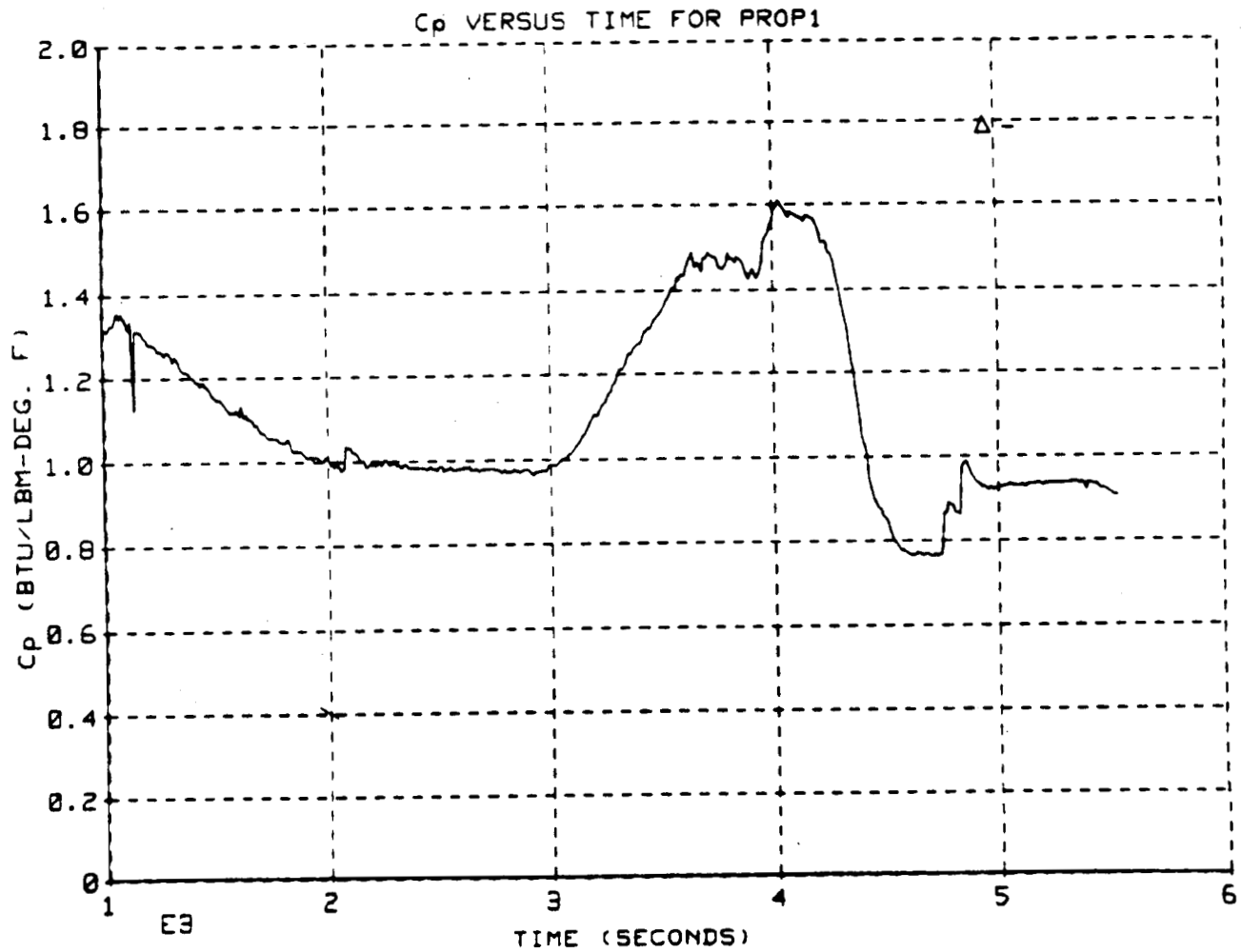


Fig. A-39 C_p vs Time for Propionaldehyde and H₂O (Run No. 11a)
(67.5% Propionaldehyde, 32.5% Water)

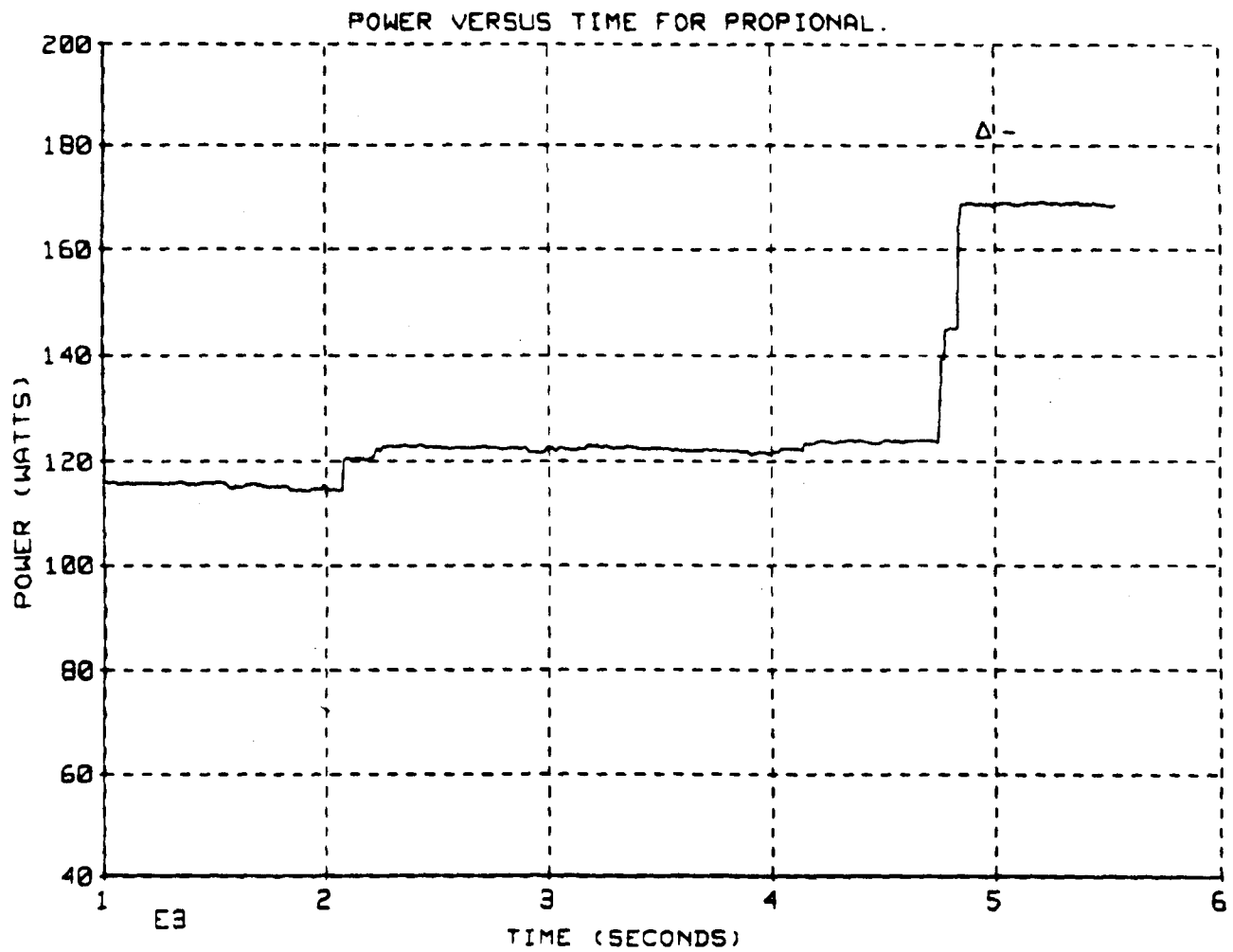


Fig. A-40 Power vs Time for Propionaldehyde and H₂O (Run No. 11a)
(67.5% Propionaldehyde, 32.5% Water)

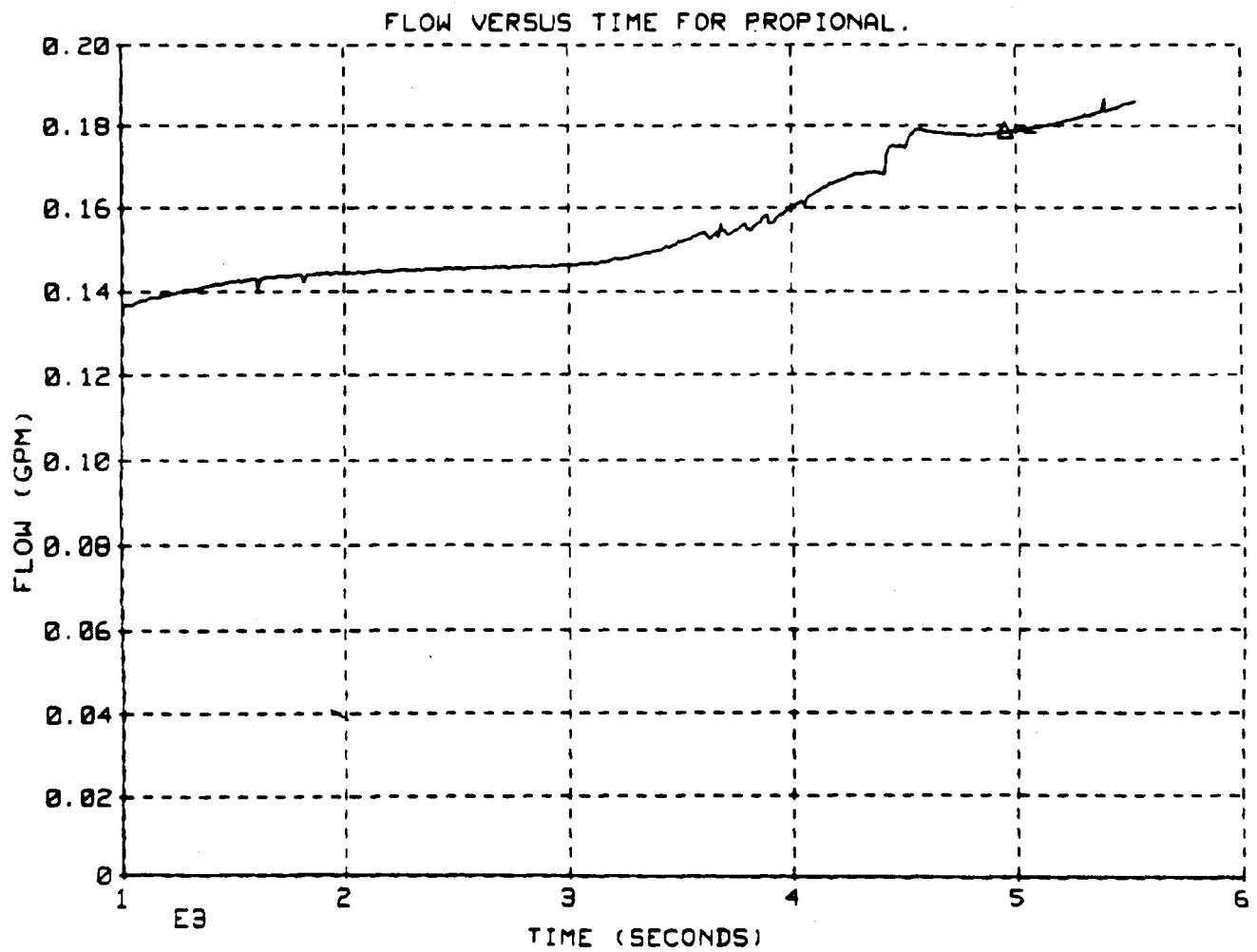


Fig. A-41 Flow vs Time for Propionaldehyde and H₂O (Run No. 11a)
(67.5% Propionaldehyde, 32.5% Water)

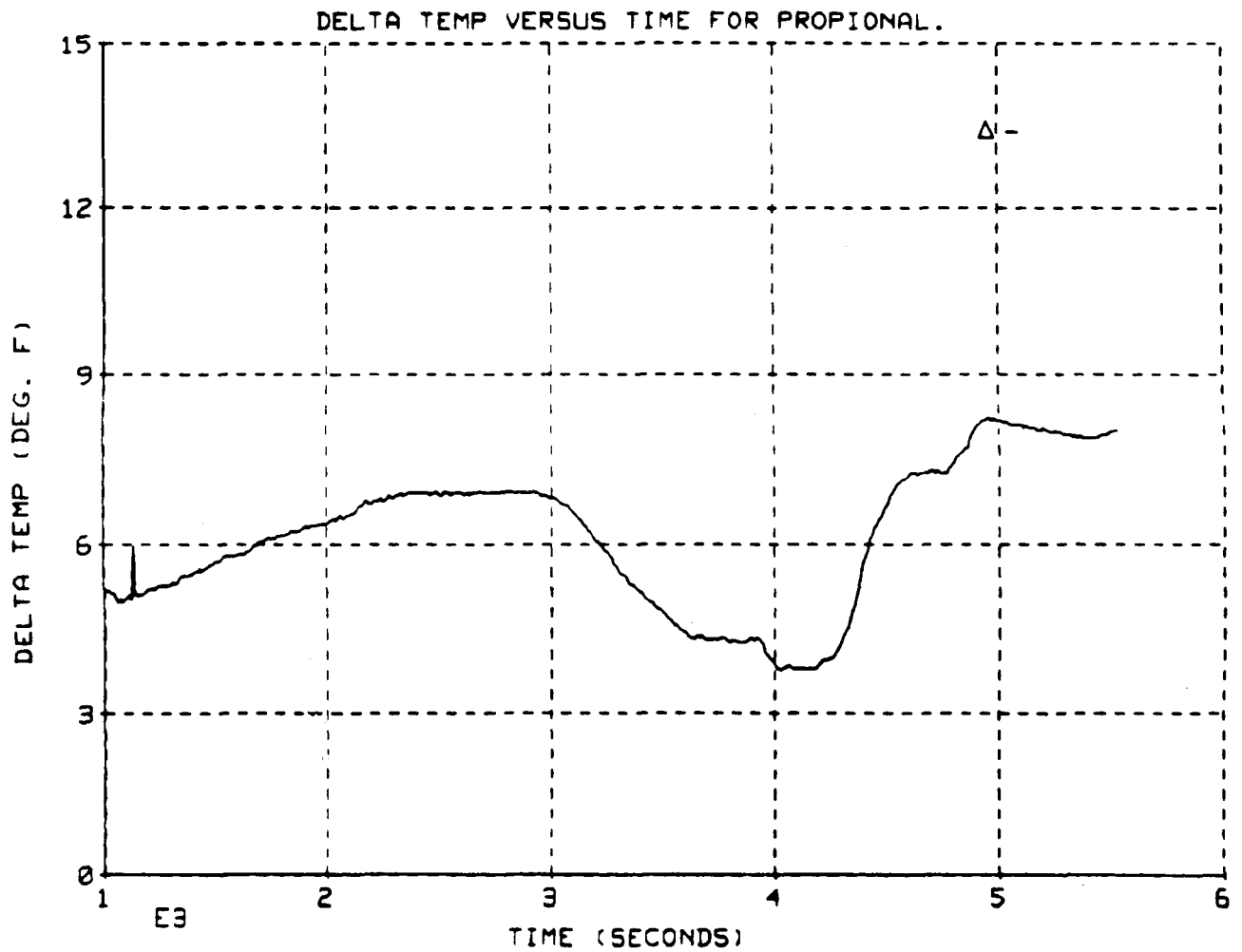


Fig. A-42 Delta Temperature vs Time for Propionaldehyde and H₂O
(Run No. 11a) (67.5% Propionaldehyde, 32.5% Water)

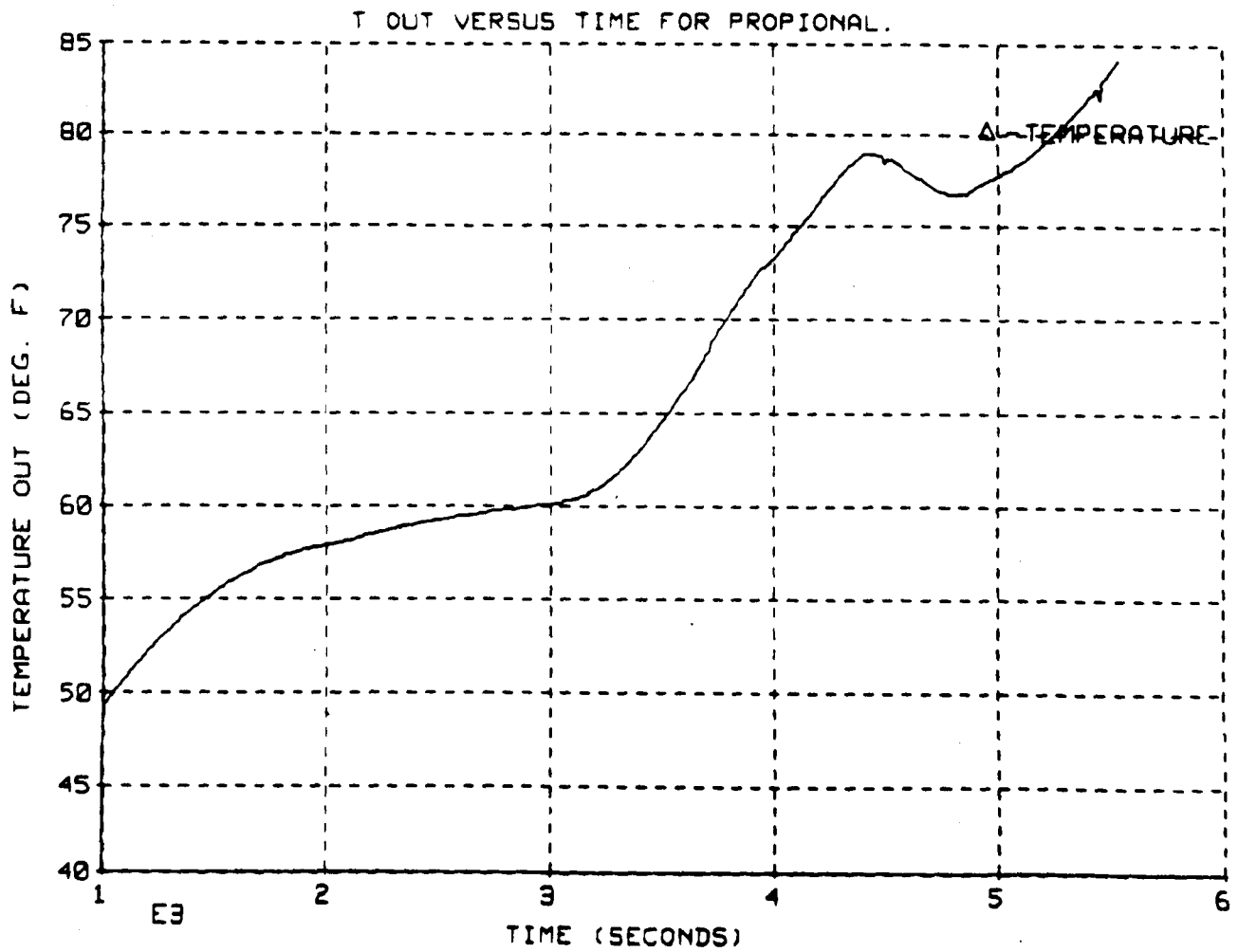


Fig. A-43 Outlet Temperature vs Time for Propionaldehyde and H₂O
(Run No. 11a) (67.5% Propionaldehyde, 32.5% Water)

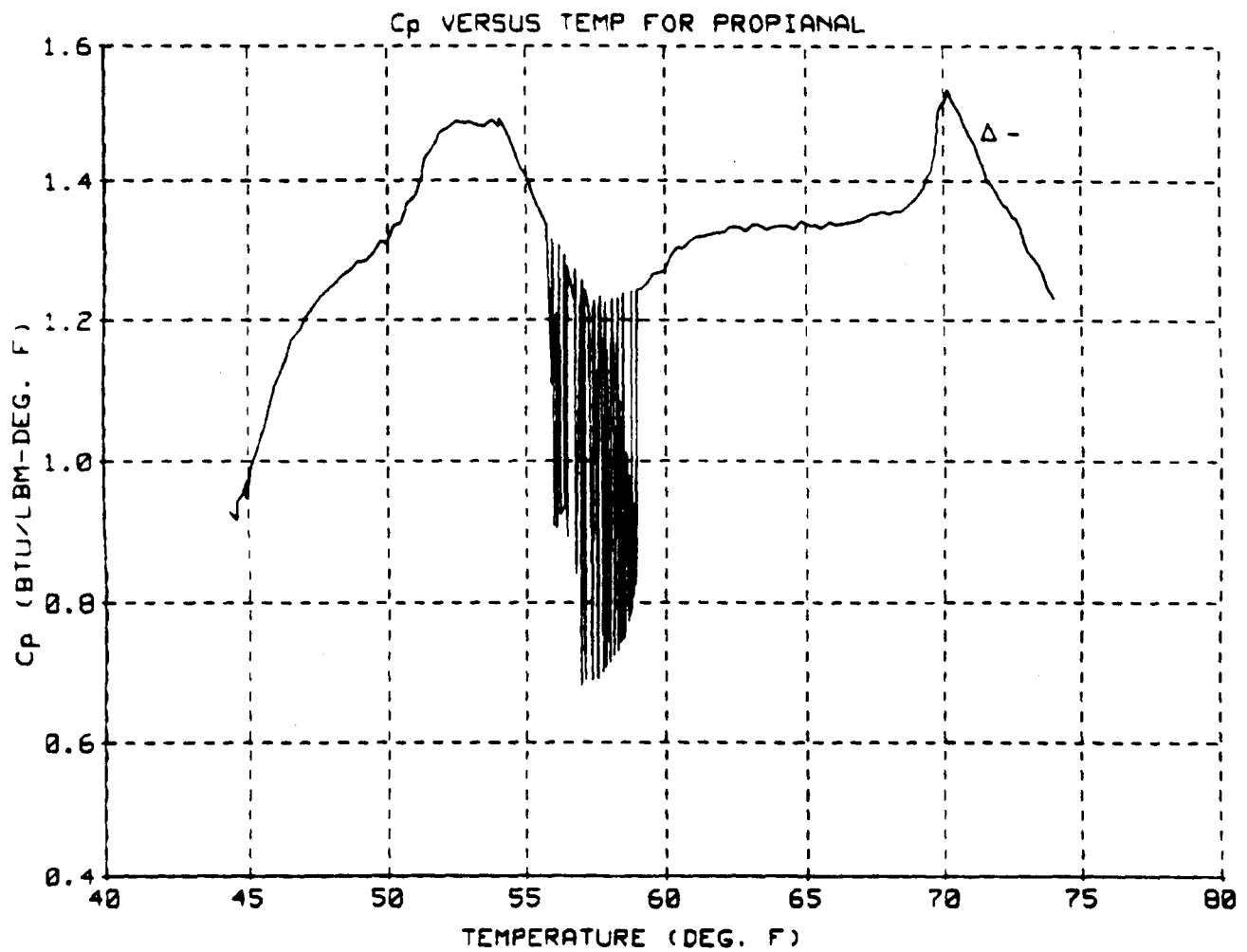


Fig. A-44 C_p vs Temperature for Propionaldehyde and Water
(Run No. 11b) (67.5% Propionaldehyde, 32.5% Water)

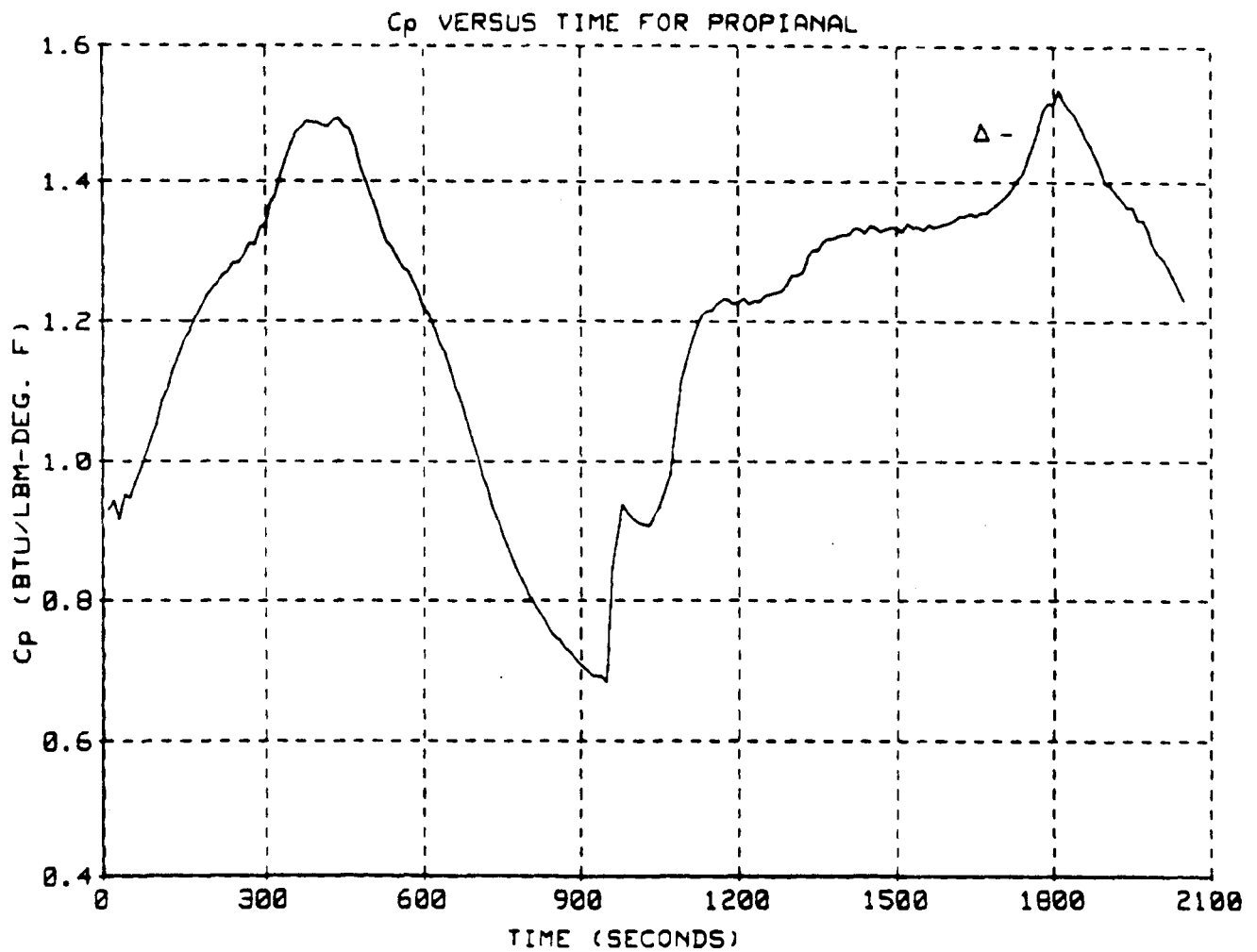


Fig. A-45 C_p vs Time for Propionaldehyde and Water (Run No. 11b)
(67.5% Propionaldehyde, 32.5% Water)

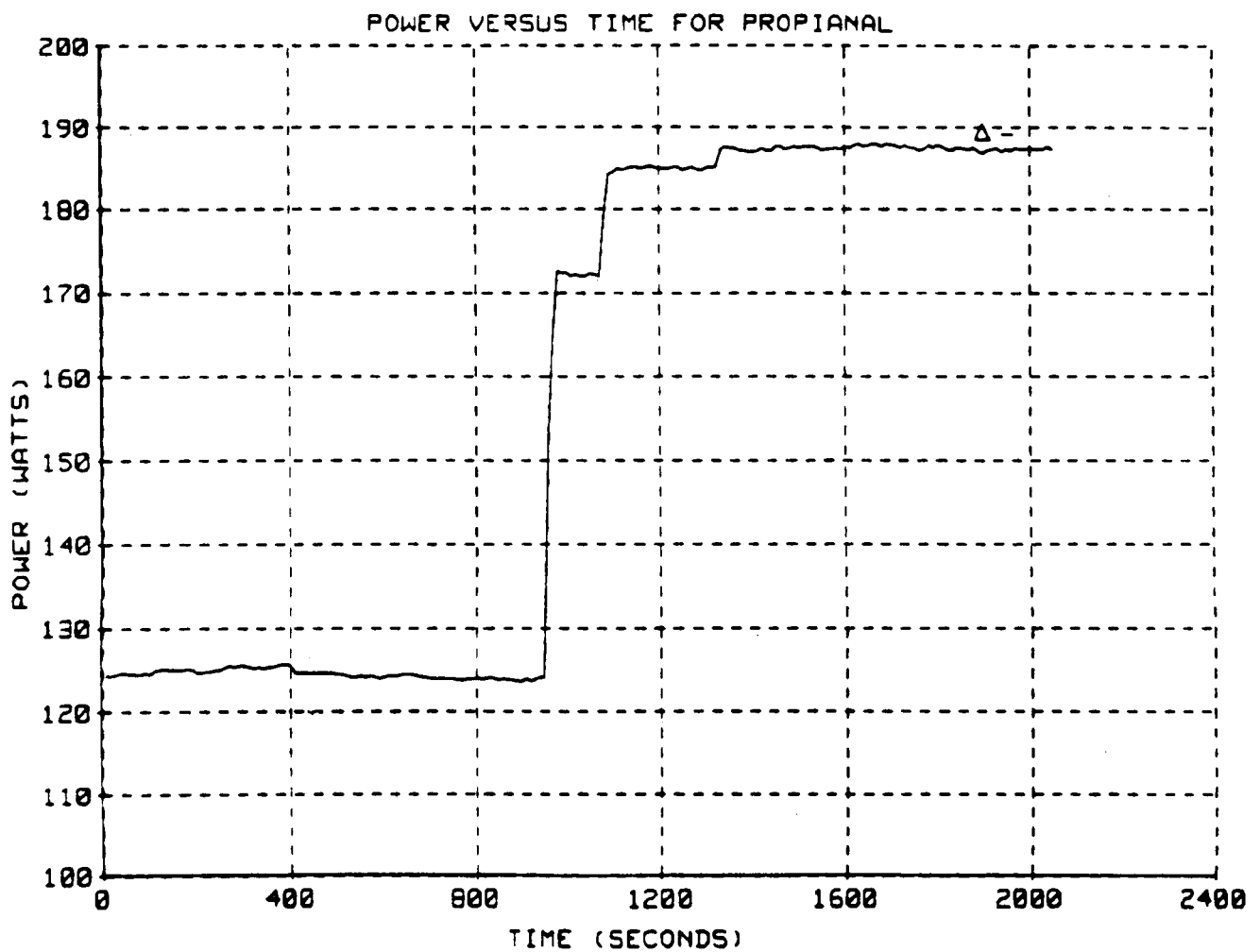


Fig. A-46 Power vs Time for Propionaldehyde and Water (Run No. 11b)
(67.5% Propionaldehyde, 32.5% Water)

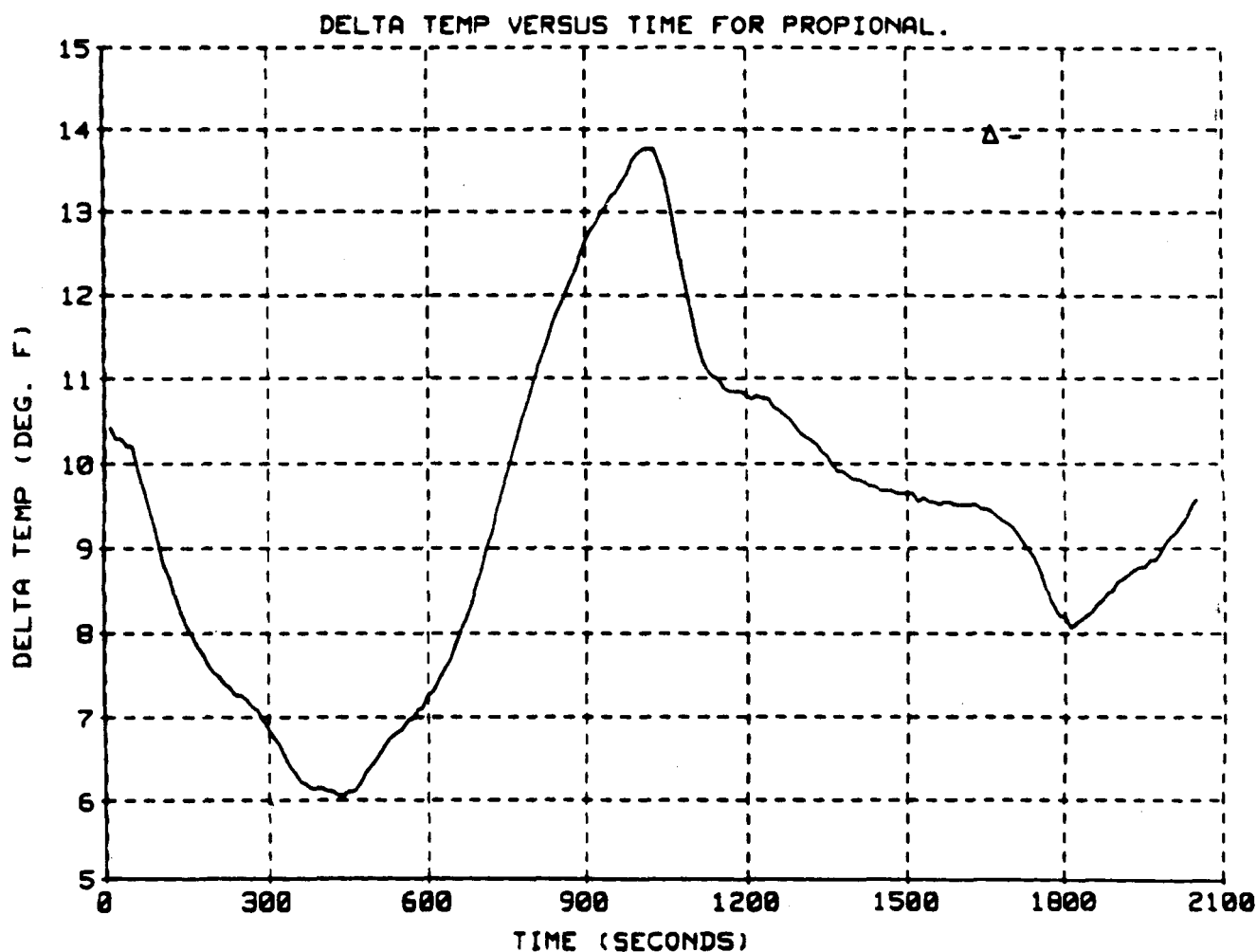


Fig. A-47 Flow vs Time for Propionaldehyde and Water (Run No. 11b)
(67.5% Propionaldehyde, 32.5% Water)

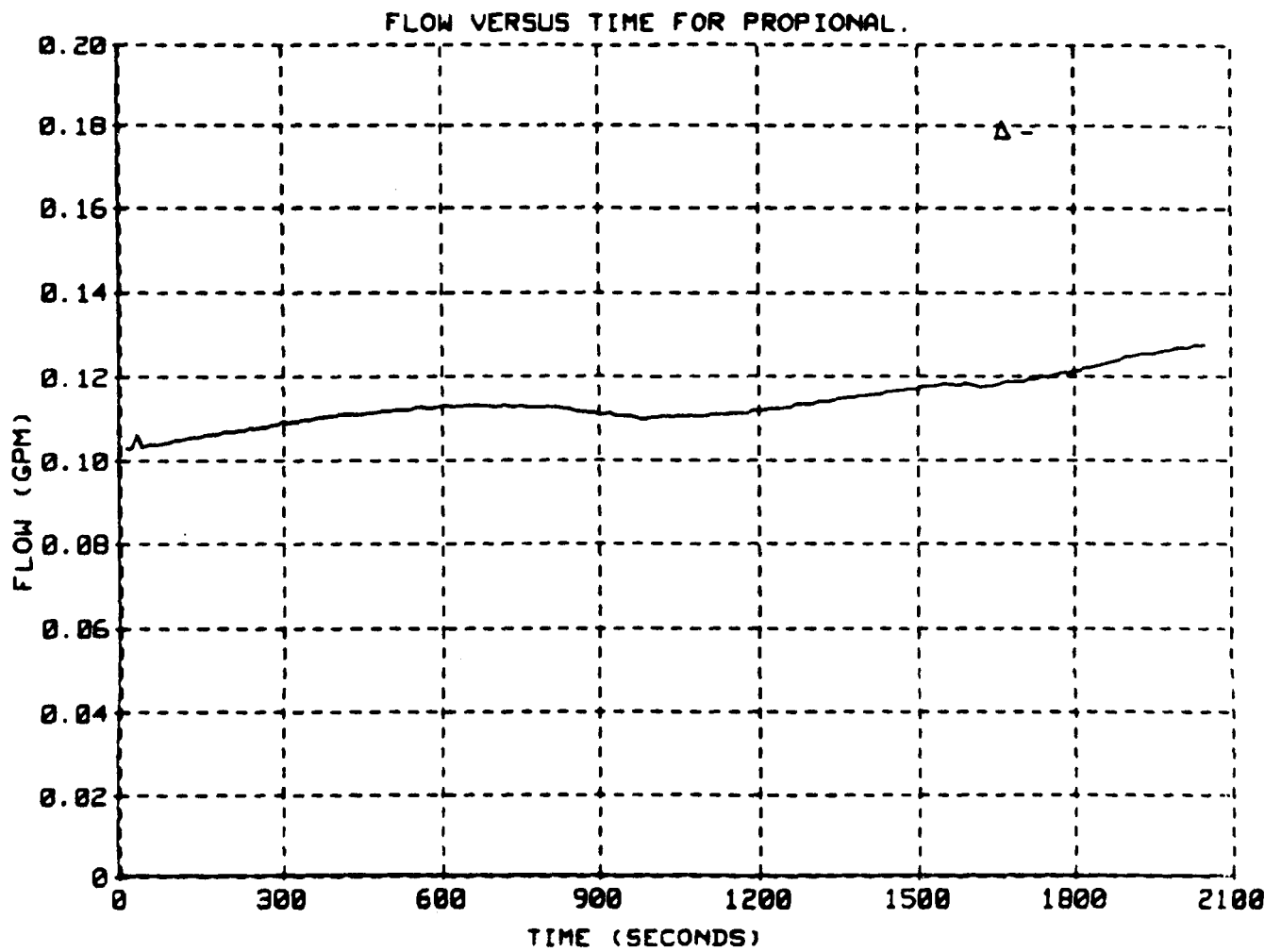


Fig. A-48 Delta Temperature vs Time for Propionaldehyde and Water
(Run No. 11b) (67.5% Propionaldehyde, 32.5% Water)

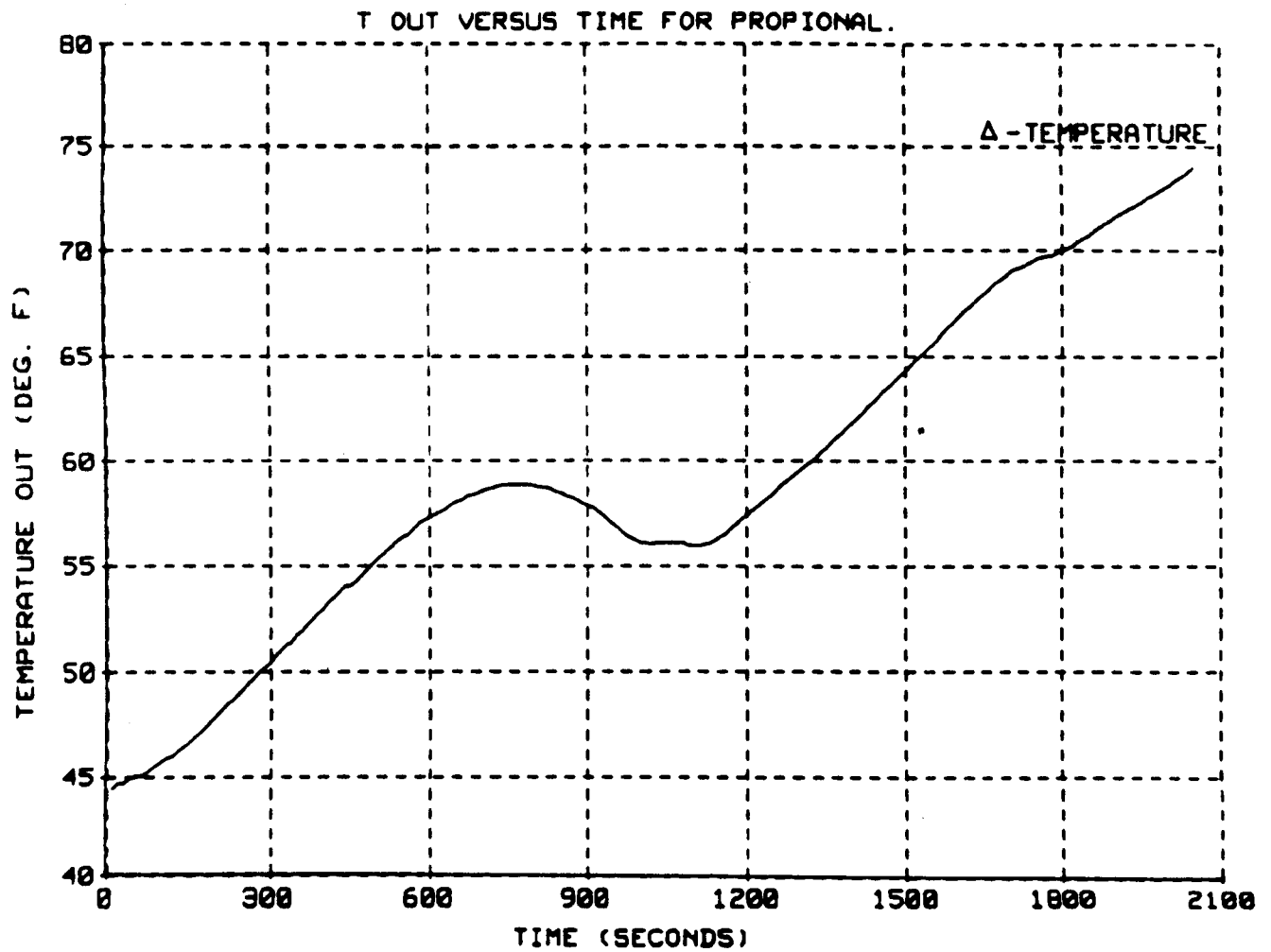


Fig. A-49 Outlet Temperature vs Time for Propionaldehyde and Water
(Run No. 11b) (67.5% Propionaldehyde, 32.5% Water)

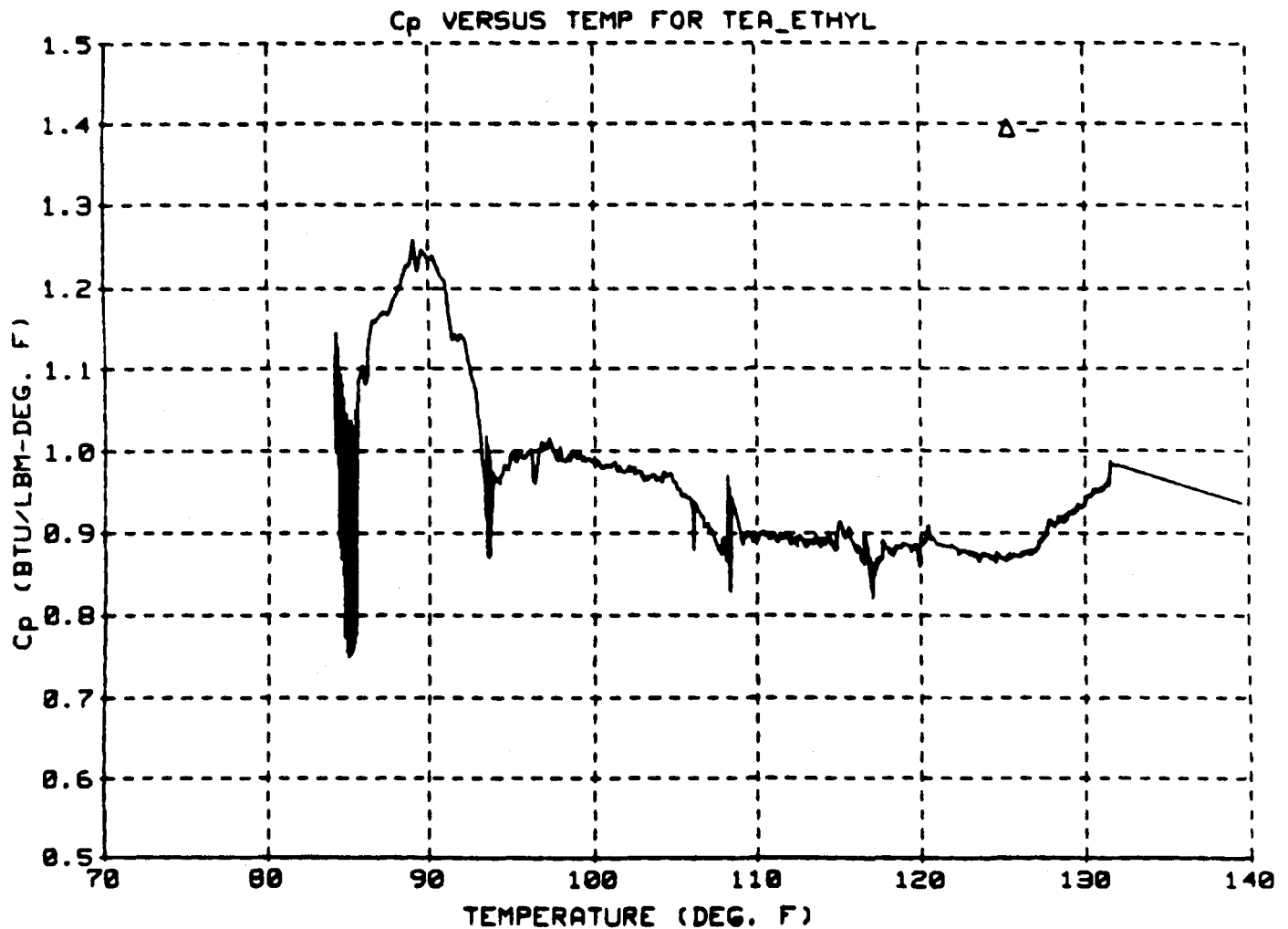


Fig. A-50 C_p vs Temperature for Triethylamine (TEA), and Ethylene Glycol (Run No. 12a) (50% Triethylamine, 50% Ethylene Glycol)

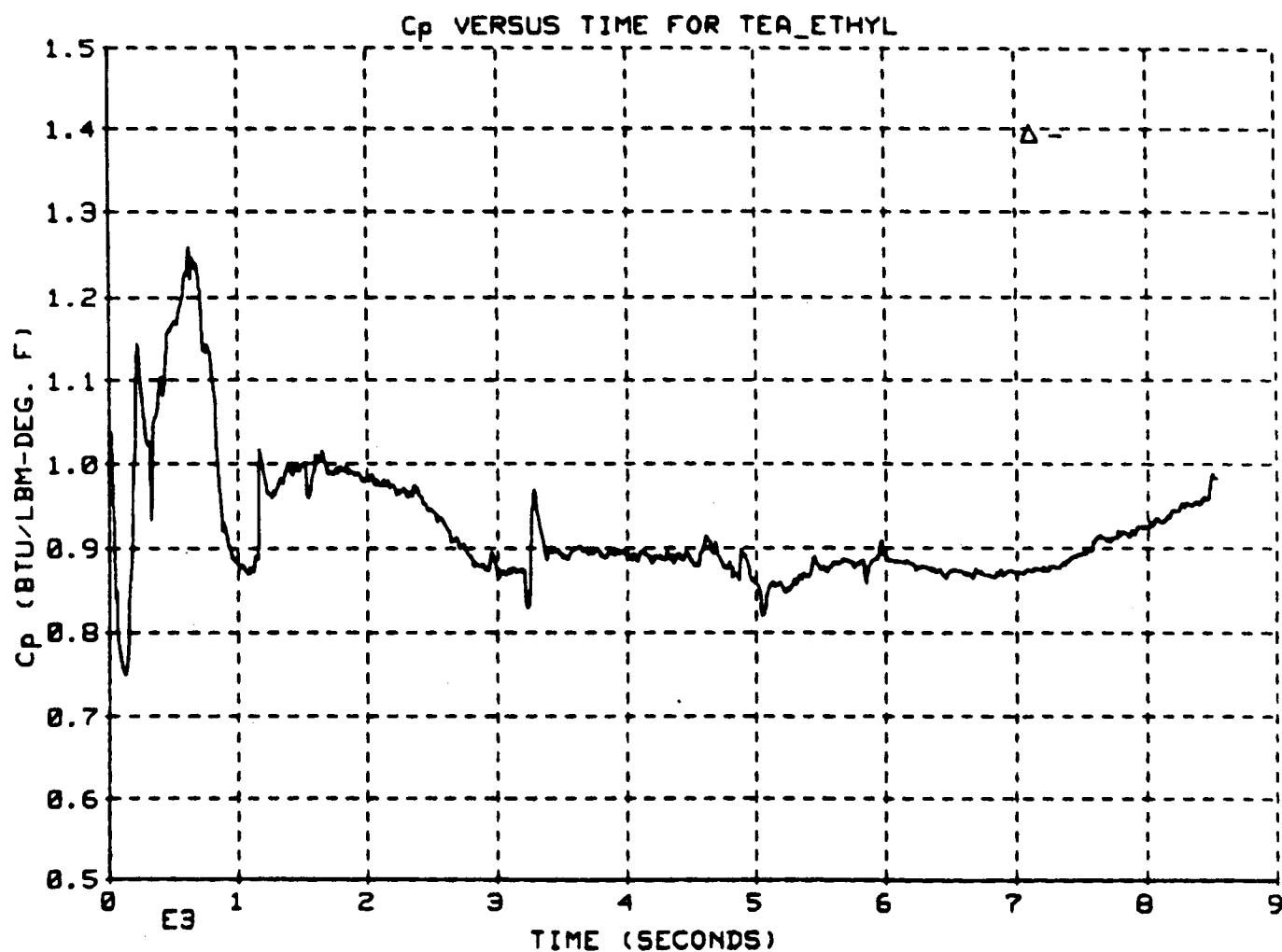


Fig. A-51 C_p vs Time for Triethylamine (TEA), and Ethylene Glycol
(Run No. 12a) (50% Triethylamine, 50% Ethylene Glycol)

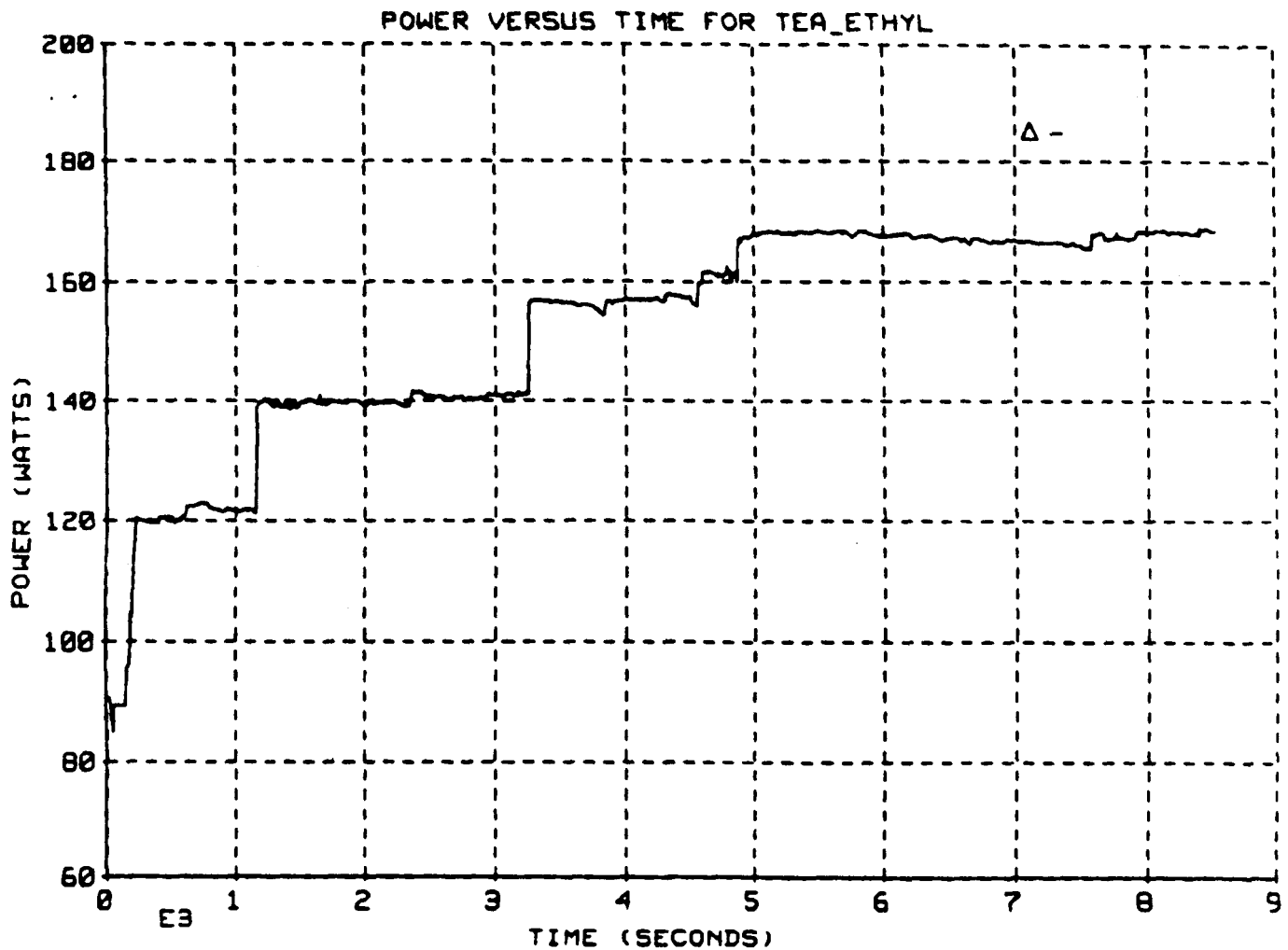


Fig. A-52 Power vs Time for Triethylamine (TEA), and Ethylene Glycol
(Run No. 12a) (50% Triethylamine, 50% Ethylene Glycol)

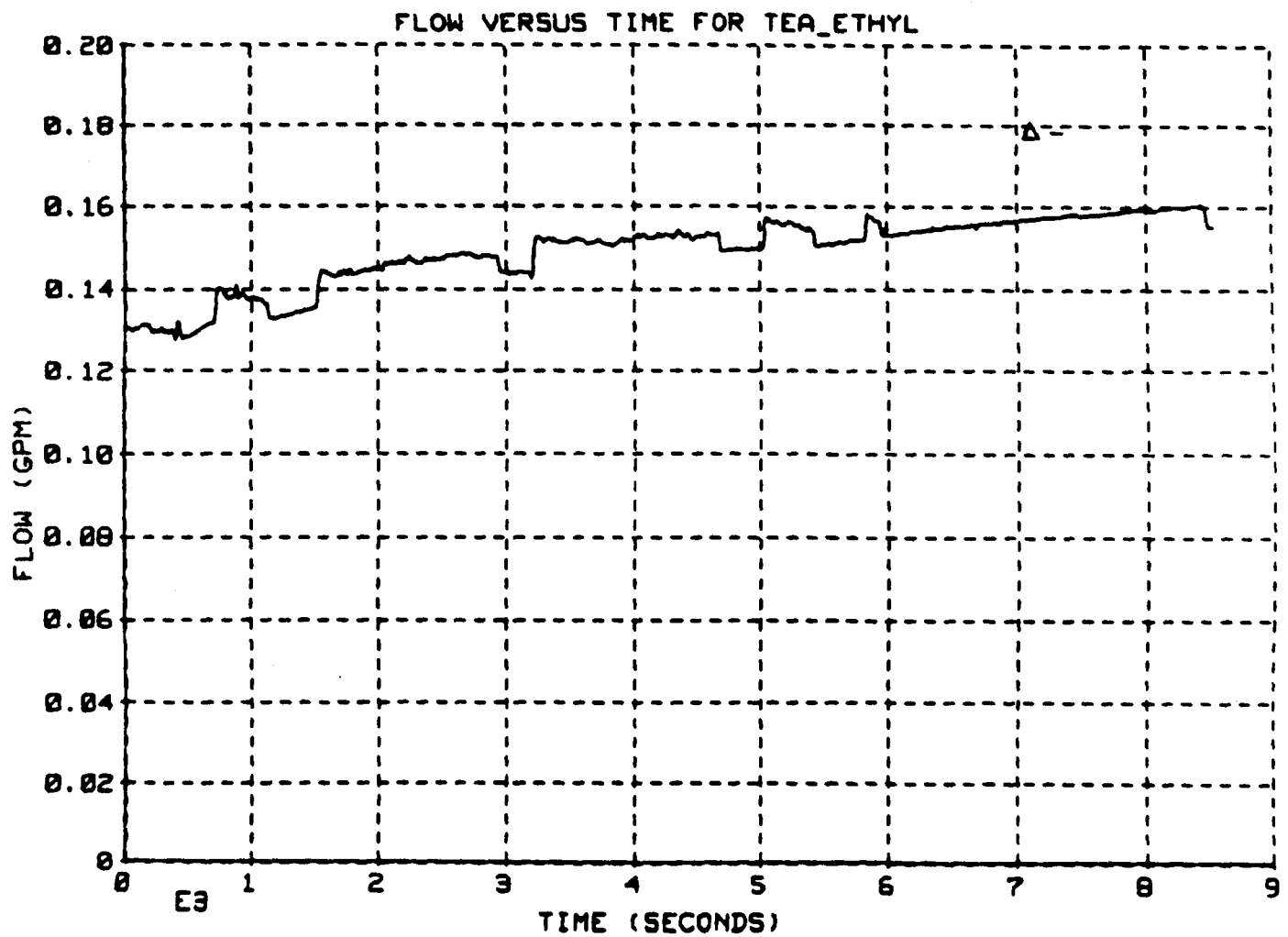


Fig. A-53 Flow vs Time for Triethylamine (TEA), and Ethylene Glycol
(Run No. 12a) (50% Triethylamine, 50% Ethylene Glycol)

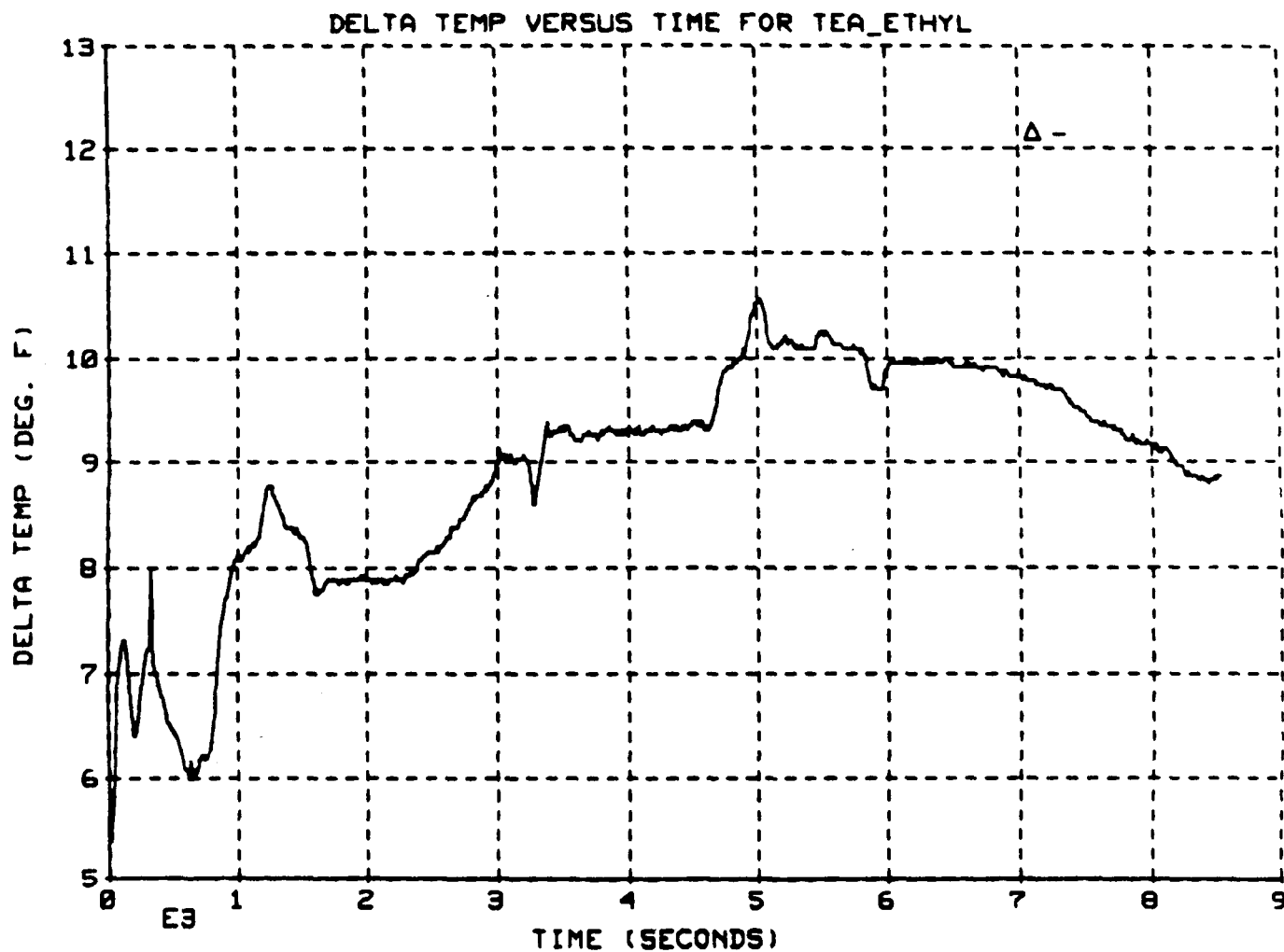


Fig. A-54 Delta vs Time for Triethylamine (TEA), and Ethylene Glycol
(Run No. 12a) (50% Triethylamine, 50% Ethylene Glycol)

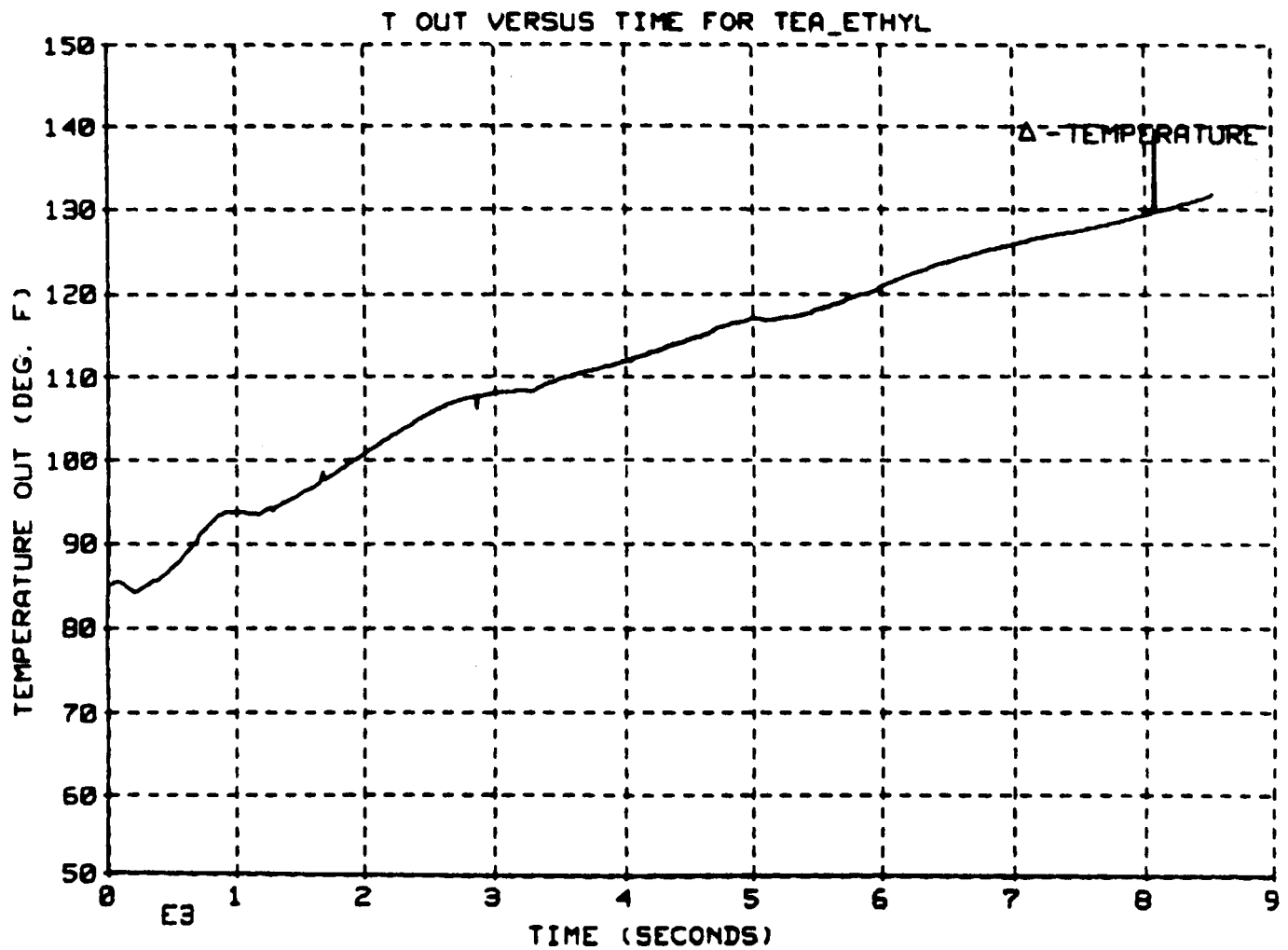


Fig. A-55 Outlet Temperature vs Time for Triethylamine (TEA), and Ethylene Glycol (Run No. 12a) (50% Triethylamine, 50% Ethylene Glycol)

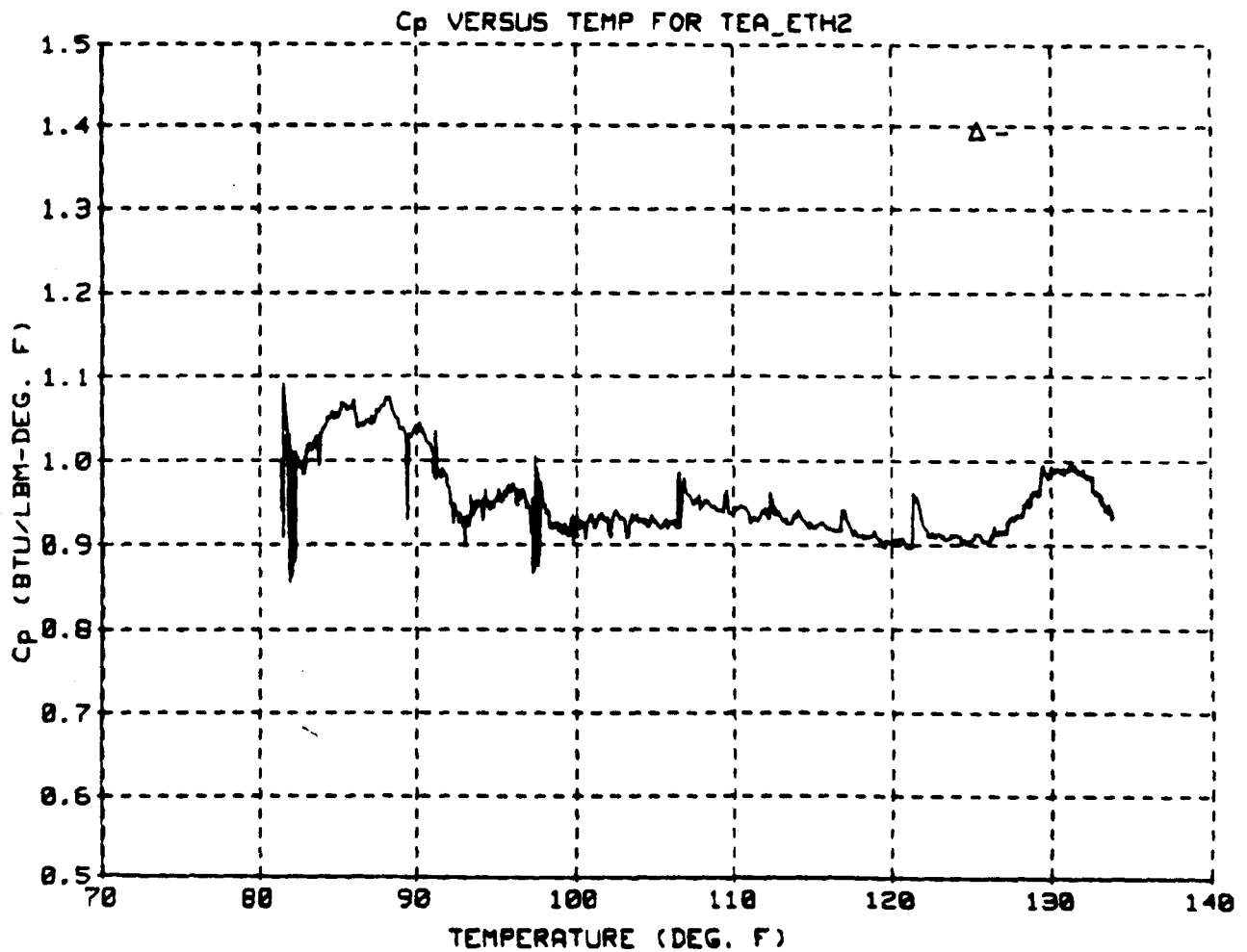


Fig. A-56 C_p vs Temperature for Triethylamine (TEA), and Ethylene Glycol (Run No. 12b) (50% Triethylamine, 50% Ethylene Glycol)

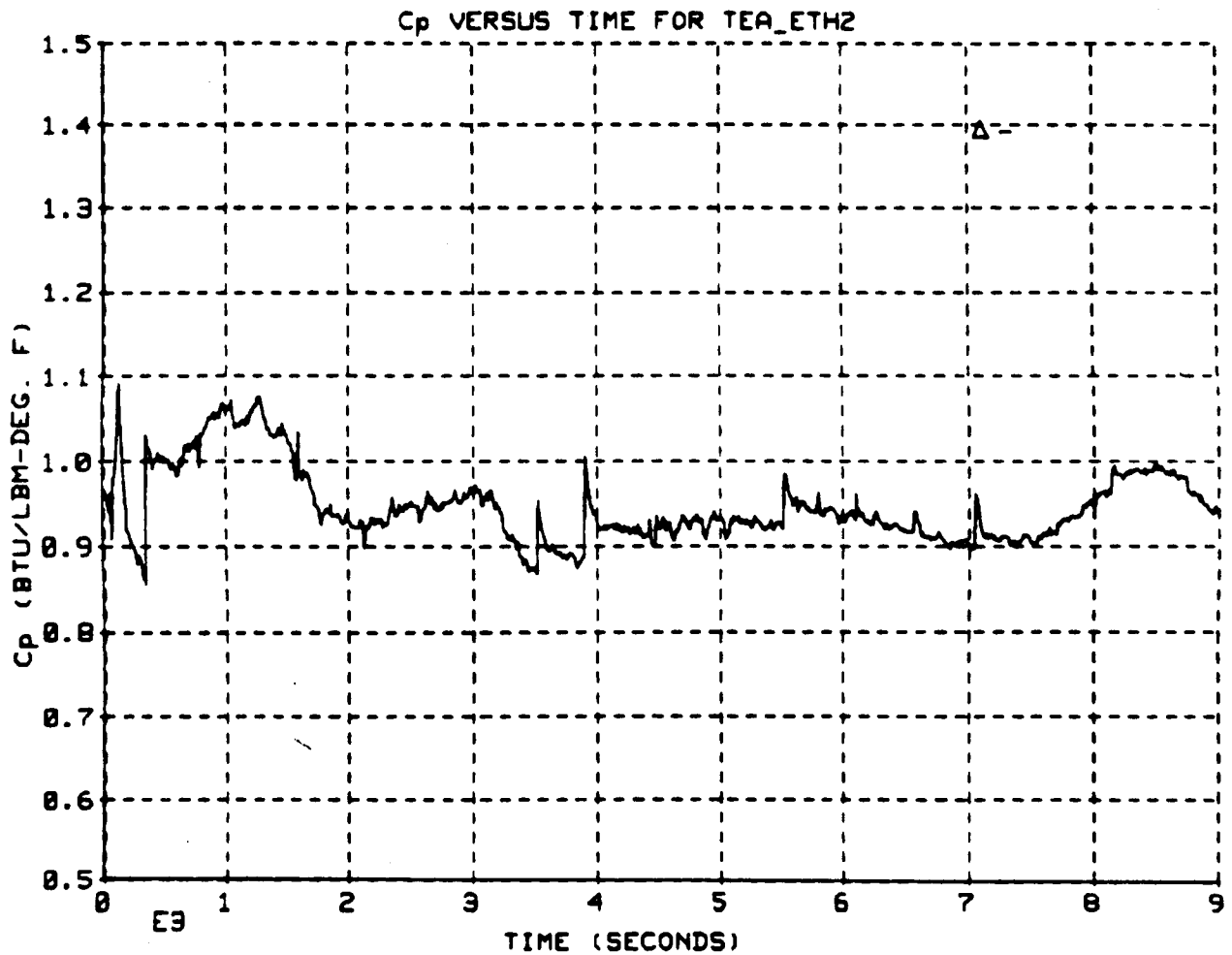


Fig. A-57 C_p vs Time for Triethylamine (TEA), and Ethylene Glycol
(Run No. 12b) (50% Triethylamine, 50% Ethylene Glycol)

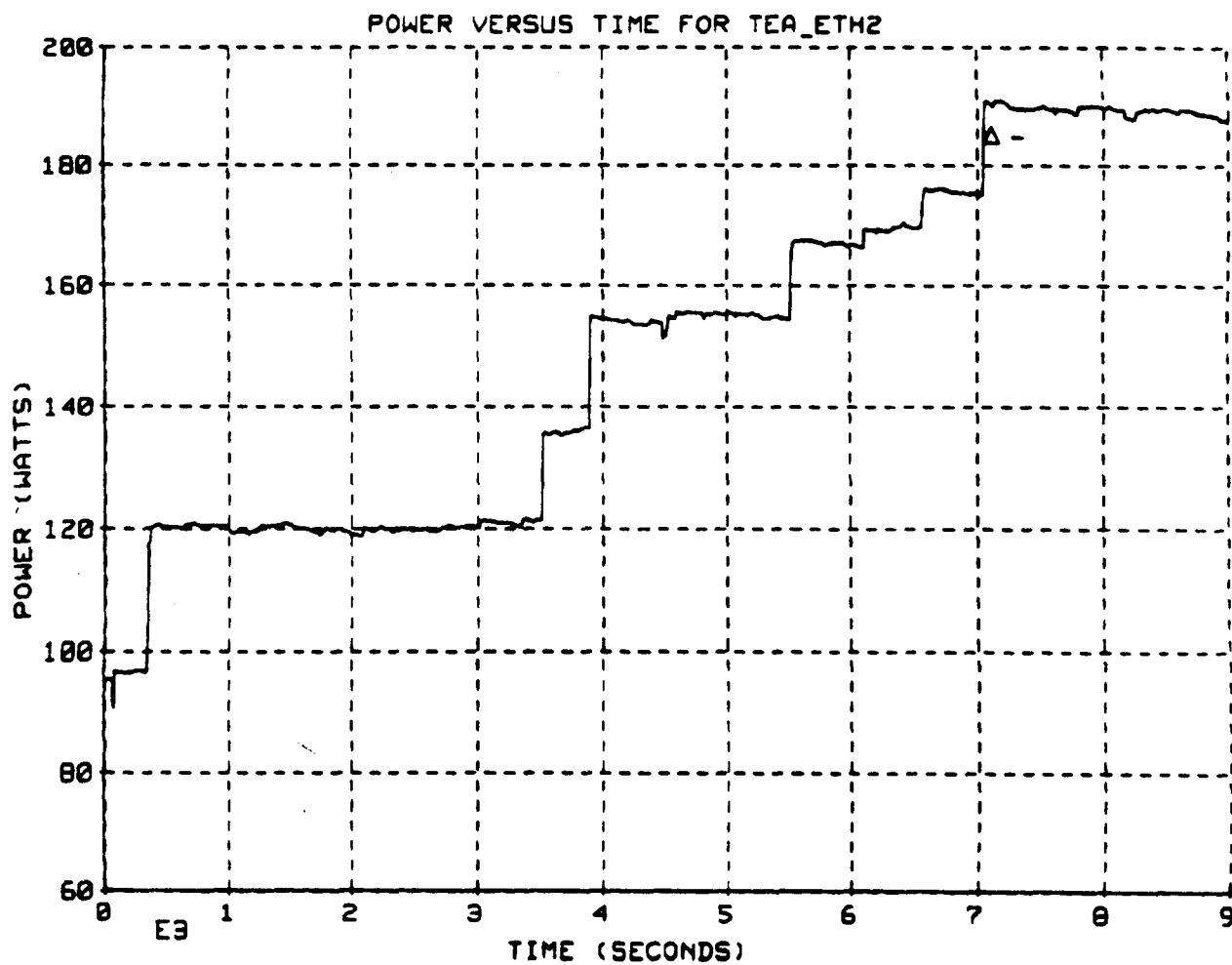


Fig. A-58 Power vs Time for Triethylamine (TEA), and Ethylene Glycol (Run No. 12b) (50% Triethylamine, 50% Ethylene Glycol)

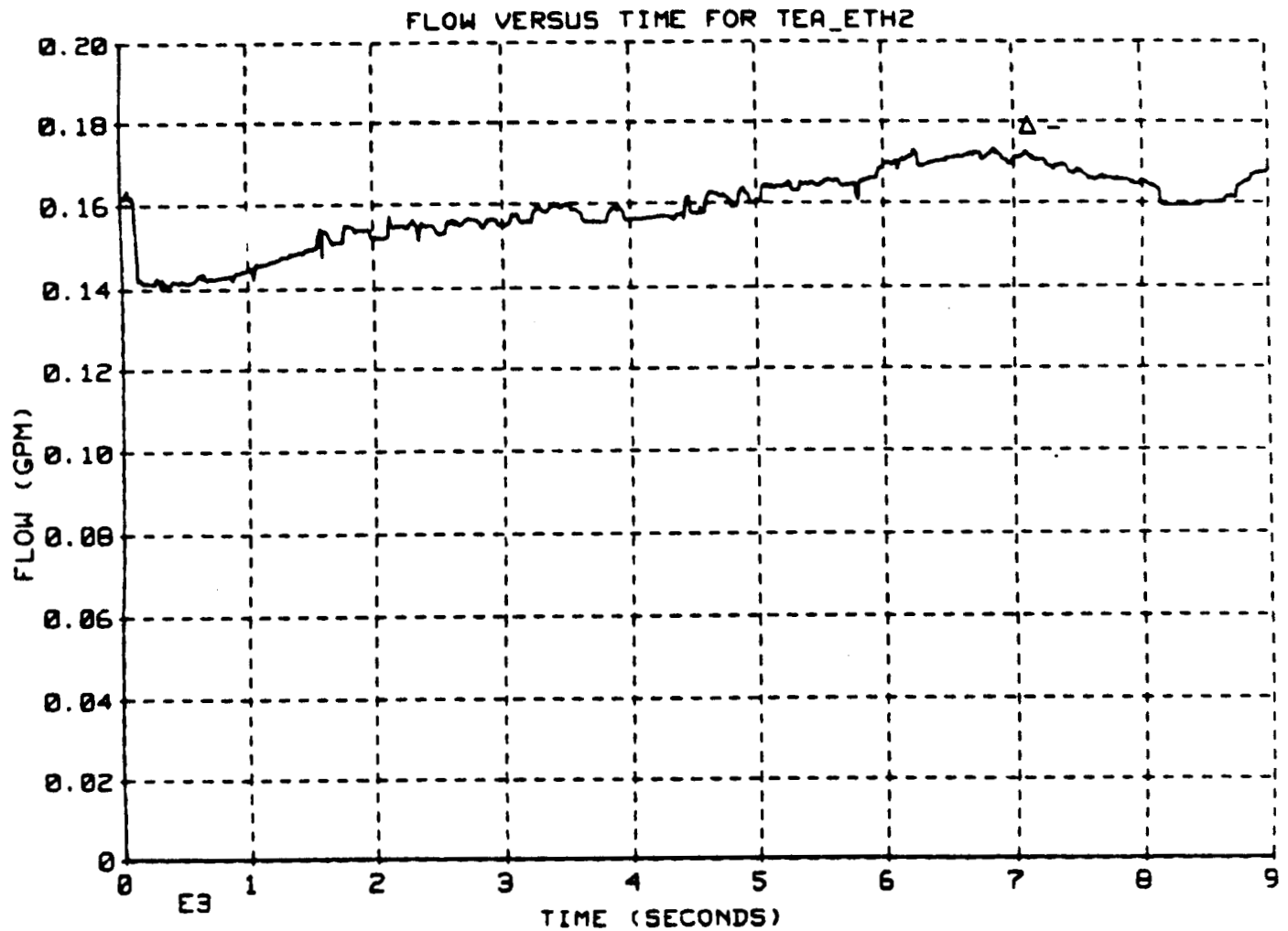


Fig. A-59 Flow vs Time for Triethylamine (TEA), and Ethylene Glycol
(Run No. 12b) (50% Triethylamine, 50% Ethylene Glycol)

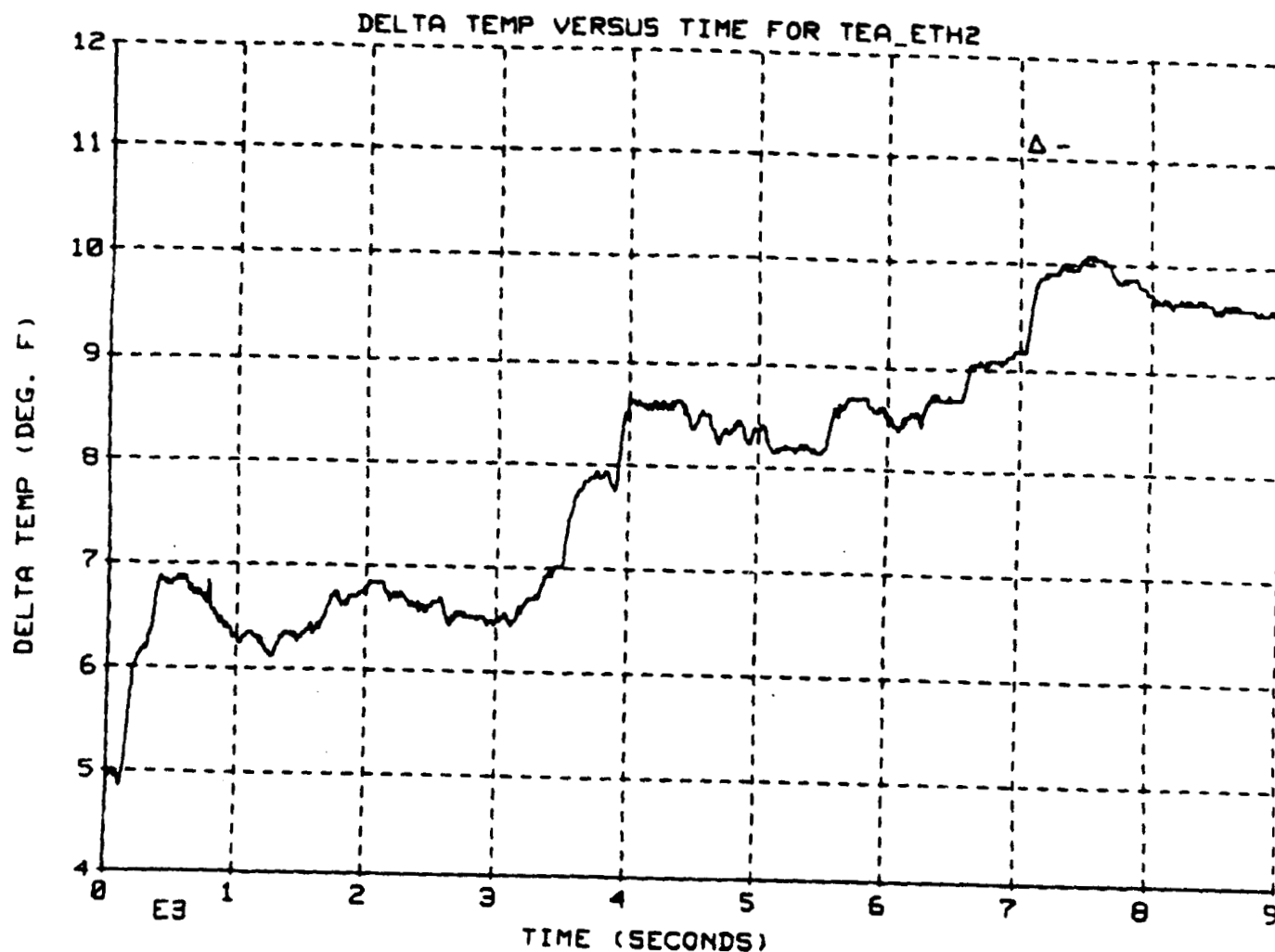


Fig. A-60 Delta Temperature vs Time for Triethylamine (TEA), and Ethylene Glycol (Run No. 12b) (50% Triethylamine, 50% Ethylene Glycol)

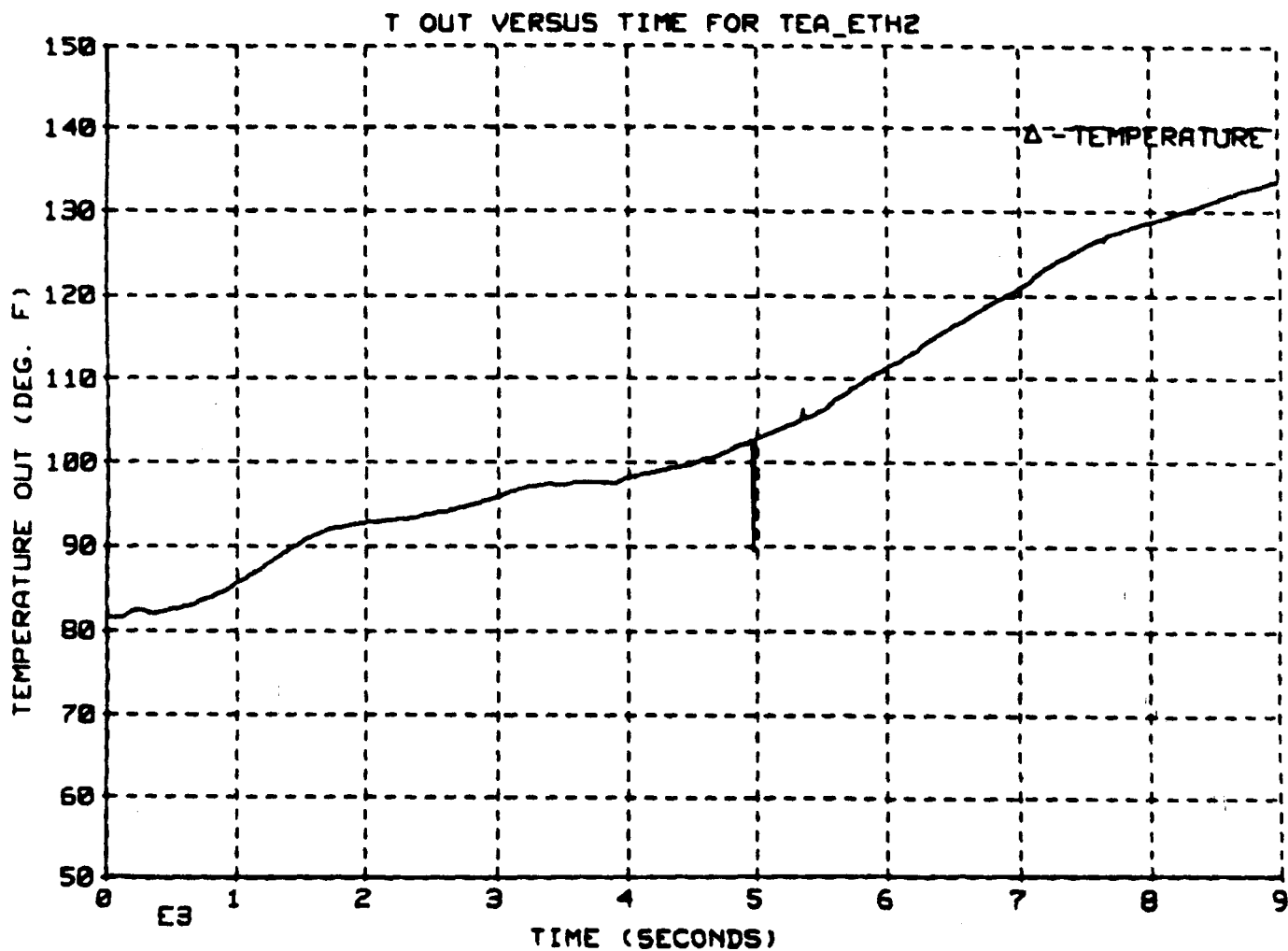


Fig. A-61 Outlet Temperature vs Time for Triethylamine (TEA), and Ethylene Glycol (Run No. 12b) (50% Triethylamine, 50% Ethylene Glycol)

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Appendix B

COPY OF PUBLISHED PAPER:

"CONJUGATING BINARY SOLUTIONS FOR SPACECRAFT THERMAL CONTROL"

International Symposium on Thermal Problems in Space-Based Systems

presented at

THE WINTER ANNUAL MEETING OF
THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS
BOSTON, MASSACHUSETTS
DECEMBER 13-18, 1987

sponsored by

THE COMMITTEE ON THEORY AND FUNDAMENTAL RESEARCH,
THE HEAT TRANSFER DIVISION, ASME

edited by

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NEW YORK UNIVERSITY

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POLYTECHNIC UNIVERSITY

THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS
United Engineering Center 345 East 47th Street New York, N.Y. 10017

FOREWORD

The diversity of fluid mechanics and heat transfer problems pertaining to the space-based systems is attested by the present volume of papers. The practical relevance of the results of these papers ranges from the design of the space station, space instruments, space vehicles and space power conversion systems to the problems involved in the space manufacturing. One of the great challenges of the future is to perfect the skills that will not only establish the man's presence in space on a more permanent basis, but also to enable him to utilize the unique features of this environment. Clearly, the technical problems are enormous and the current symposium volume is an effort to bring together the research efforts pertaining to the heat transfer in space-based systems. The range of problems considered in the papers includes: super heat pipe design considerations and transient testing; transient conduction effects in target plates due to the high power laser irradiation and the low temperature radiometer design considerations; theoretical and experimental investigations of forced convection condensation with suction at the wall and gas-liquid flow pattern identification under the microgravity conditions of space; design of boiling heat transfer and flow separation experiments for space; the use of general purpose fluid mechanics and heat transfer programs for the design of space station and other space vehicles; liquid metal magnetohydrodynamic two-phase flow power conversion system analysis; crystal manufacturing in a microgravity environment; and analysis of heat transfer problems associated with the space plane and fluid behavior under a rapid depressurization to the vacuum of space.

The editors wish to express their appreciation to all the authors who submitted abstracts and papers for the symposium. We also wish to acknowledge the help of reviewers whose efforts have improved the quality of the papers. Our special thanks are extended to the Innovative Science and Technology Directorate of the Strategic Defense Initiative Organization which provided partial support for widely advertising the purpose and scope of this international symposium.

Flavio Dobran
Murray Imber

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CONJUGATING BINARY SOLUTIONS FOR SPACECRAFT THERMAL CONTROL

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Lockheed-Huntsville Engineering Center
Huntsville, Alabama

J. W. Owen

NASA-Marshall Space Flight Center, Alabama

ABSTRACT

A concept for spacecraft thermal control systems has recently emerged that depends on the heat of mixing of a pair of different liquids at a critical solution temperature. Liquid pairs that mix (or unmix) at a critical solution temperature are called conjugating binary systems. As the liquids mix or unmix, heat is absorbed or released, resulting in a high effective specific heat over a small temperature interval.

Use of a conjugating binary system for heat transfer in a spacecraft promises several advantages. Because of the high effective specific heats, significant reduction of pumping power requirements over conventional liquid Freon systems may be possible. Also because of the nature of the variation of heat capacity as a function of temperature, a conjugating binary system can provide some self-regulating thermal control without an active control system. The total liquid character of conjugating binary systems promises further significant advantages over gas-liquid or liquid-solid two-phase systems in space: the avoidance of expensive zero-g flight tests and experiments of phase separation concepts, and elimination of heat transfer obstruction on solid surfaces. Conjugating binary materials can be chosen to undergo liquid-liquid phase change at almost any desired temperatures. They thus offer versatility for a variety of applications.

A report of a preliminary demonstration of the concept is given as well as the results of a further study involving the identification of practical conjugating binary liquids.

NOMENCLATURE

C_p = specific heat, J/g-K

D = diameter of tube, m

\dot{m} = mass flow rate, g/s

P = pumping power, W

\dot{Q} = heat transferred, W

L = length of tube, m

T = Temperature, K

$\Delta T = T_2 - T_1$ (K)

t = time, s

ρ = density, g/m³

μ = dynamic viscosity, Pa.s

Subscripts

1 = inlet

2 = outlet

INTRODUCTION

Motivation for Technology Development

Active Spacecraft Thermal Control (STC) utilizes heat transport systems that acquire heat from sources (components and experiments) and move the heat to spacecraft radiators or sinks. The state of the art for such thermal transport systems is pumped liquid systems with appropriate feedback control (Shuttle technology). A major disadvantage for this type of system is that as the magnitude of heat increases, the required system flow rate must increase. This, in turn, can require a large pump which utilizes significant electrical power. For very large sys-

tems, the power penalty is unacceptable. For this reason, recent technology development programs have addressed more efficient methods of accomplishing the heat transport function.

Several projects are under way to develop two-phase (liquid-to-vapor) thermal transport systems. These systems take advantage of the large latent heat of vaporization of the working fluid. The fluid evaporates at the heat sources, the vapor is transported to the heat sink where it condenses, and the resulting liquid is pumped back to the heat sources forming a closed cycle. The disadvantages of these concepts appear to be the complex problem of managing the liquid and vapor phases in zero gravity. On the ground, the phase separation occurs due to buoyancy, but this does not happen in the spacecraft environment. For this reason complex fluid management and control systems are required to guarantee that the liquid and vapor flows are maintained properly.

Ideally, the thermal transport system would exhibit a large latent heat without inducing phase separation and fluid management difficulties. This would require a liquid-to-liquid, reversible phase transformation with an attendant release of energy, analogous to the solid-to-solid lattice phase transformations exhibited by some solids. Such liquid-to-liquid phase transformations are not known to exist. A promising concept is currently under study, however, which exhibits characteristics similar to a solid-solid phase transformation.

The concept depends upon the heat of solution of a pair of liquids at a critical solution temperature (CST). Liquid pairs that combine (or dissociate) at a CST are called conjugating binary (CB) systems. The CB concept appears attractive for STC systems because relatively high heats of mixing may be obtained entirely within the liquid phase. The concept under study would utilize a CB pair as the working fluid of a thermal transport system. Because of the high heat of mixing (or dissociation), the fluid pair would exhibit a very high specific heat or thermal capacitance. This characteristic would allow a small mass flow rate (to transport a given amount of heat) and greatly reduce the electrical energy required to operate the system.

Review of Physico-Chemical Principles

The ideal conjugating binary fluid system would exhibit a phase diagram as shown in Figure 1. In this ideal system the two phases, A and B, would be totally immiscible until the critical solution temperature, t_c , is reached. At this temperature, the two phases would form a one-phase solution. The total heat of mixing would be realized at the critical solution temperature. Actual systems do not behave in this fashion, but show deviations from the ideal as shown in Figures 2 and 3. These departures result in wider temperatures intervals being required to realize sizable heats of mixing.

To gain an understanding of the separation processes that occur in a real CB system, consider Figure 4 which represents the phase diagram of a binary liquid system composed of fluids A and B. If the system is initially at t_2 (above the CST) the system would be fully mixed and appear, visually, to be one liquid. As the system is cooled to t_c , two liquid phases, one rich in A (C_1) and one rich in B (C_2), begin to separate from the original solution.

Differences in density cause a stratification to occur. Upon sufficient cooling the reaction will be driven to completion and the system will consist entirely of solution C_1 separate from solution C_2 . During the process a significant heat of dissociation should have been realized. Table 1 presents typical values of the CST and heat of mixing for known CB systems.

Further considerations and discussions of the physico-chemical principles involved are given in earlier reports and papers [1-6].

Nature of Research and Development Being Reported

A demonstration of the CB thermal control principle was accomplished with a small experimental test loop and a CB that was identified in earlier studies as promising. Based on these results, a comprehensive laboratory test program was undertaken. The purpose of this program was to quickly identify and characterize as many candidate fluid pairs as possible.

CONCEPT DEMONSTRATION

A simple test apparatus was devised for the purpose of verifying the concept validity [7]. A schematic of this system is shown in Fig. 5, and a photograph of the test set-up in the laboratory is shown in Fig. 6. In this loop, the CB is pumped from the ice bath to the heat source. Heat is supplied to the circulating fluid by means of resistance heating. During a run, a known amount of heat is added to the circulating fluid and the temperatures T_1 and T_2 are monitored. Knowing the flow rate, the temperature of the ice bath, the temperatures T_1 and T_2 , and the amount of heat added to the circulating liquid, the effective heat capacity of the circulating CB can be calculated by use of the following equation:

$$\dot{Q} = \dot{m} C_p \Delta T$$

The specific heat as a function of temperature was determined by slowly increasing the inlet and outlet temperatures by means of increased heat transfer rate.

Specific heat as a function of temperature thus determined for a triethylamine (TEA) - water solution (32% TEA/68% Water, all percentages being weight percents) is shown in Figure 7. The first series of tests, indicated by the symbol Δ , started at an inlet temperature T_1 above 9.4 C and terminated at 13.3 C, at which temperature the phase change was observed to be complete. The second series of tests, indicated by the symbol \circ , started at a higher inlet temperature T_1 , i.e., 11.1 C and ended at 21.1 C.

The data of Figure 7 show that an effective heat of 105 J/g can be achieved from 8.9 to 21.1 C, for an average specific heat of 8 J/g over this interval. Freon-type coolant typically have specific heats on the order of 0.84 J/g-K.

A simple calculation considering only the thermal and density fluid characteristics, indicates that a CB system having an effective C_p of approximately 8 J/g-K would decrease the pumping power requirement to maintain a given heat transfer rate by a factor of 380, as compared to Freon. An additional factor needs to be considered, however, and that is

the viscosity of the solution over the temperature interval in which the phase change occurs. CB materials generally undergo increases in viscosity as a result of solution. For example, some measured viscosities of CB solutions near the critical solution temperature and of the component liquids are given in Table 2.

The data show that the viscosity of a CB solution is approximately a factor of 2 to 4 above that of the pure component liquids, although the absolute values of the solution viscosities for the CBs investigated are still quite low.

Increases in viscosity as the result of CB phase change, however, are judged at this point to have a minor effect on pumping power requirements, as deduced from the following derived equation:

$$P \sim \left[\frac{\mu}{C_p} \right]^{0.25} \left[\frac{\dot{Q}}{\Delta T} \right]^{2.75} \frac{L}{D^{4.75}}$$

The exponential dependencies of μ and C_p predict that any increase in C_p would substantially outweigh a viscosity increase.

MATERIALS SEARCH

While literature surveys and experience can lead to families of candidate fluid pairs (aromatic hydrocarbons, halogenated compounds, amines, etc.), the number of potential combinations is enormous. When coupled with spacecraft fluid system requirements (low freezing temperature, high boiling point, relatively low CST, non-toxic, etc.) the research effort becomes quite challenging.

The search strategy consists of two parts: (1) identifying CBs likely to have high heats of mixing and critical solution temperatures in the temperature range of approximately 5 C to 50 C, and (2) subjecting identified CBs to a quick screening test. CBs that perform well in the quick screening test become candidates for further testing in the test loop.

Identification of CBs for quick screening is not a trivial task. Only very limited CST and heat of mixing data exist in the literature, and a general theory for reliably and easily predicting CSTs and heat of mixing is lacking. Prediction of CST and heat of mixing by means of theory or computer models is possible if it can be ascertained that the mixing reaction does not involve hydrogen-bonding. Non-hydrogen-bonding CBs, however, are of little interest for present purposes because the heats of mixing for such systems have been found to be too low to be of use for thermal control purposes.

In the course of exploratory work, a knowledge base was built up that served to guide the search [8]. This knowledge base derives from reported works dealing with solubility parameters and hydrogen-bonding. The paper on solvent selection by means of miscibility number by Norman B. Godfrey [9], was particularly helpful as a practical guide. In this paper, Godfrey reports the results of miscibility tests with some 400 different organic solvents. He was able to assign a miscibility number, M, to each solvent which generally reflected its lipophilicity (affinity for oil-like substances). He found that if

the M-number of two liquids differ by 15 units or less, the two liquids are miscible in all proportions at 25 C. If the M-number difference is 16, the two liquids have a critical solution temperature between 25 C and 75 C. An M-number difference of 17 or more indicates immiscibility or a critical solution temperature above 75 C. Unfortunately, Godfrey did not consider the effect of hydrogen-bonding on miscibility prediction. His categorization, however, was very helpful in eliminating a number of combinations from consideration or in limiting the number of combinations tried. On the basis of the literature and Godfrey's M-number paper, a selection of liquids was obtained for experimentation. These are given in Table 3 along with M values.

A number of simple mixing tests were run with various combinations of the liquids obtained. In these tests small approximately equal amounts of liquids were mixed at room temperature and the heat effect noted by means of an immersed thermocouple. If the liquids mixed gave a temperature rise, the solution was heated to see if separation occurred. If the liquids mixed gave a temperature fall, the solution was cooled to see if separation occurred. If no mixing occurred, the contacted liquids were both heated and cooled to see if mixing would occur. In this manner a great deal was learned about classes of liquids and some new likely CBs discovered. In addition to such CB identification studies, studies on the effect of the addition of a third component are also being performed. The purpose of the additive is either to adjust the CST to a more desirable level or to depress the freezing point of the mixture. Candidate CBs selected for further screening are subjected to a quick screening test, the nature of which is as follows.

To start a test (two identical flasks, as shown in Figure 8) are plunged into the circulating fluid, constant temperature bath. One of the flasks contains the reference material (water) and the other CB candidate.

The temperature of both flasks and the bath during the test are monitored by means of RTDs. Assuming a valley type CB, the CB and reference temperatures generally rises as shown in the Figure 9.

The temperature at which the CB curve begins to show a significant change of rate is approximately the CST. The extent to which the CB curve continues to change slope is an indication of the heat effect involved. By measuring the slopes of the water and CB curves at the same temperatures, an approximate C_p of the CB can be obtained. The rationale for this procedure is embodied in the following equality:

$$\left(mC_p \frac{dT}{dt} \right)_{CB} = \left(mC_p \frac{dT}{dt} \right)_{H_2O}$$

By means of computer, the time-temperature data are readily reduced to a specific heat versus temperature plot. The data thus reduced are rather ragged because of stirring of the liquids is not adequate in this simple apparatus. An averaging technique helps some. Some unaveraged and averaged data for the system triethylamine and water are presented in Figure 10. The experimental material studies conducted thus far indicate that the following two classes of liquid-liquid interaction offer the most promise of containing CB candidates:

Intermolecular Hydrogen-Bonding: Valley-type CBs are the result of extensive hydrogen-bonding between the two component liquids and have been found to exhibit the largest realizable mixing heats. CB candidates thus far identified in this category include triethylamine/salt solution, N-cyclohexyl-2-pyrrolidone/4 percent sodium chloride solution, and propylene glycol mono-t-butyl ether/water.

Intramolecular Hydrogen-Bonding: Upper CST systems were initially dismissed rather early in the study because two test cases (isobutyric acid/water and propylene carbonate/water) showed only slight enhancement of fluid heat capacity in the quick screening tests. As our knowledge of the nature and role of hydrogen-bonding in liquid-liquid mixing grew, however, it was realized that one subcategory of this class should be explored further. This subcategory is one in which one of the liquids is highly self-associated through intramolecular hydrogen-bonding and the other acts as a neutral non-bonding carrier. In this type system, heating causes intramolecular hydrogen-bonding to weaken, i.e., causes the self-associated liquid to become dissociated. The dissociated liquid then mixes in a normal fashion with the non-bonding carrier liquid. A prime example of this type system is the epichlorohydrin/n-heptane system. A quick screening test showed that this system indeed holds promise as a practical CB.

Other combinations within this subcategory that should be explored are amides, halogenated alcohol, and other potentially intramolecularly bonded liquids with neutral carriers. A number of such tests are currently under way.

CONCLUSIONS AND FUTURE STUDIES

The concept of increased heat capacity under practical, transient thermal conditions by means of conjugating binaries has been demonstrated. In addition, CBs in which intermolecular or intramolecular hydrogen-bonding are the predominant interactions involved in the mixing processes were found to be most likely to have high enough heats of mixing to be of interest for practical applications.

Future studies indicated included testing of CBs identified by the quick screening test in an improved version of the initial heat transfer test loop; further exploration of liquid combinations holding the promise of extensive intermolecular or intramolecular hydrogen-bonding; improving the stirring mechanism in the quick screening apparatus; and the development of a quick screening technique would allow the exploration of materials that need to be tested under pressures somewhat greater than atmospheric.

ACKNOWLEDGMENTS

Paul M. McCormick of Lockheed-Huntsville contributed substantially to the concept development and experimental studies. He derived the engineering equations and consulted on the experimental design and data reduction of the test loop and quick screening technique.

Messrs. Zain Karu and Jeff Hammett conducted the experimental tests with the test loop.

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Table 1 TYPICAL CONJUGATING BINARIES

CB	(Wt.% A/Wt.% B)	CST, K (C)	Approximate Heat of Mixing J/g of Solution
Triethylamine/Water	(38/62)	291 (18)	60
Isobutyric Acid/Water	(35/65)	298 (25)	52
Propanal/Water	(63/37)	289 (16)	
Methanol/Cyclohexane	(28/72)	318 (45)	16
Methanol/Cyclohexane	**	290 (17)	20.9
n-Butoxy-Ethanol/Water	**	322 (49)	
Methanol/Carbon Disulfide	(20/80)	309 (36)	14
Succinonitrile/Ethanol	**	301 (28)	
Aniline/Cyclopentane	**	291 (18)	
Aniline/Cyclohexane	**	303 (30)	21

** Not found in the literature

Table 2 MEASURED CB VISCOSITY VALUES NEAR CRITICAL SOLUTION TEMPERATURES

CB System	Composition (Wt %)	Critical Solution T (K)	T of Viscosity Measurement (K)	μ Solutions (10^3 Pa.s)	μ Pure Liquids at Same Temps. (10^3 Pa.s)	
					Org	Water
Triethylamine/ Water	38/62	291	276, 288	7.92, 4.89		1.1618, 1.139
Isobutyric Acid/Water	35/65	303	309	1.69	0.711	0.705
Propanal/Water	68/32	289	288	2.43		1.139

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Table 3 EXPERIMENTAL LIQUIDS

Abbrevi- ation	Liquid	Godfrey Number	Abbrevi- ation	Liquid	Godfrey Number
AA	Acetic Acid	14	2EEA	2-Ethoxy Ethylacetate	15,19
AC	Acetone	15,17	2(EO)E	2-(2-Ethoxy Ethoxy)- Ethanol	13
AN	Aniline	12	ECEL	2-Ethoxy Ethanol (Ethyl Cellosolve)	14
BA	n-Butyl Acetate	22	EG	Ethylene Glycol	2
BCAR	Butyl Carbitol (Diethylene Glycol Monobutyl Ether)		MCEL	Ethylene Glycol Monomethyl Ether (Methyl Cellosolve)	13
BCEL	Butyl Cellosolve (Ethylene Glycol Monobutyl Ether, 2-Butoxyethanol)	16	EP	1-Ethylpiperidine	3
BE	Butyl Ether	26	FORM	Formamide	
BCHO	Butyraldehyde		DPK	4-Heptanone (Butyrone, Dipropylketone)	23
ISOB	Isobutyric Acid	16	HP	Heptane	29
NBOH	n-Butyl Alcohol	15	HX	1-Hexanol	17
TBOH	Tert. Butyl Alcohol (2-methyl-2-propanol)		LUT	2, 6 Lutidine	
BL	γ-Butyrolactone	10	NMF	N-Methyl Formamide	
CS2	Carbon Disulfide	26	NMP	N-Methyl Pyrrolidone	13
CHX	Cyclohexane	28	NEP	N-Ethyl Pyrrolidone	
CP	Cyclopentane		CHP	N-Cyclohexyl- 2-Pyrrolidone	
CLEOH	2-Chloroethanol	11	HEP	N-(2-Hydroxyethyl)- 2-Pyrrolidone)	
2CLE	Dichloroethane (Ethylene Dichloride)	20	PYR	Pyrrole	
2CLM	Dichloromethane	20	MEOH	Methanol	12
3CLE	Trichloroethylene	20	MEK	Methyl Ethyl Ketone	17
4CLE	Tetrachloroethylene (Perchloroethylene)	25	MEA	Monoethanolamine	2
DEG	Diethylene Glycol	5	PCHO	Propionaldehyde	
DEA	Diethanolamine	1	1PROH	1-Propanol	15
DEC	Diethyl Carbonate	21	2PROH	2-Propanol	15
DEK	Diethyl Ketone	18	PA	Propyl Acetate	19
DES04	Diethyl Sulfate	12,21	PC	Propylene Carbonate	9,17
DMA	N, N-Dimethyl- acetamide	13	PTB	Propylene Glycol Mono-t-Butyl Ether	
DMF	Dimethyl Formamide	12	PYRI	Pyridine	16
DMOS	Dimethyl Sulfoxide	9	TEOSI	Tetraethylortho- silicate	23
EC	Ethylene Carbonate	6,17	SUCC	Succinonitrile	
EDA	Ethylene Diamine	9	TEOA	Triethanolamine	2
EOH	Ethanol	14	TEA	Triethylamine	26
EPICL	Epichlorohydrin	14,19	TOL	Toluene	23

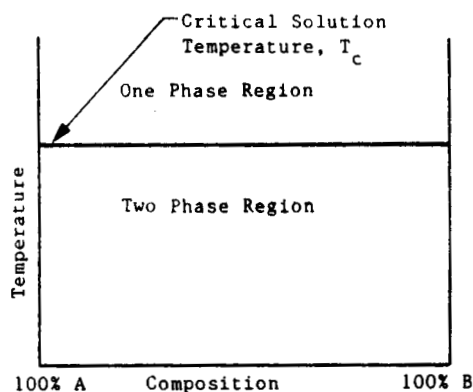


Figure 1 Phase Diagram for an Ideal CB

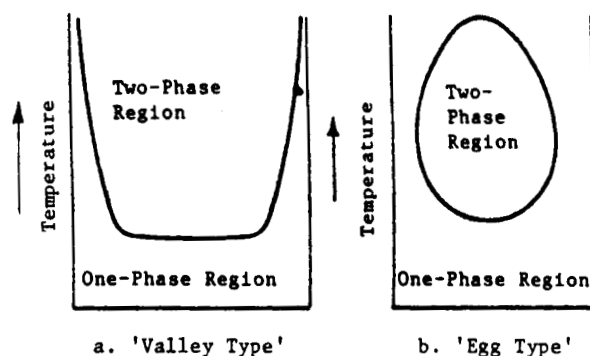


Figure 3 Phase Diagram for Further Types of CBs

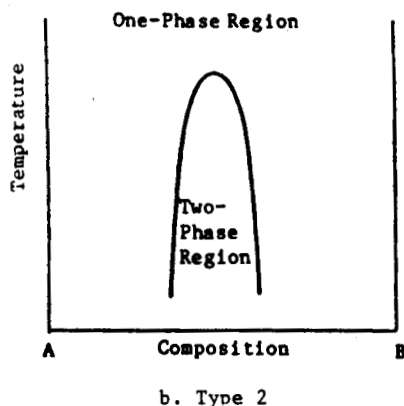
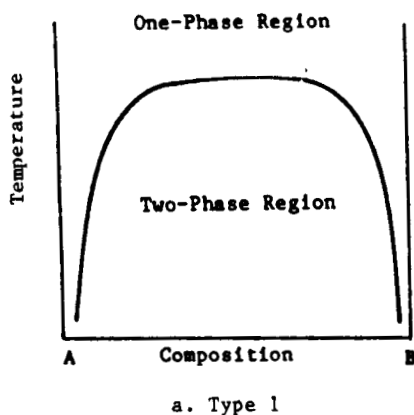


Figure 2 Phase Diagram for Real CBs Showing 'Hill Type' Immiscibility

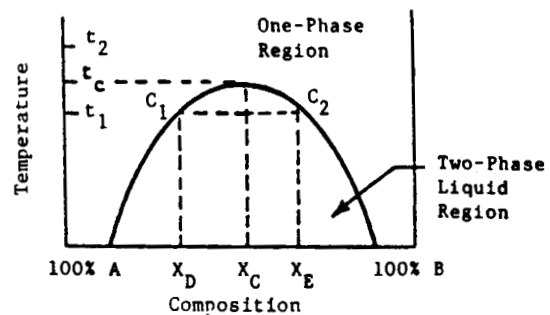


Figure 4 Phase Representative 'Hill Type' Diagram

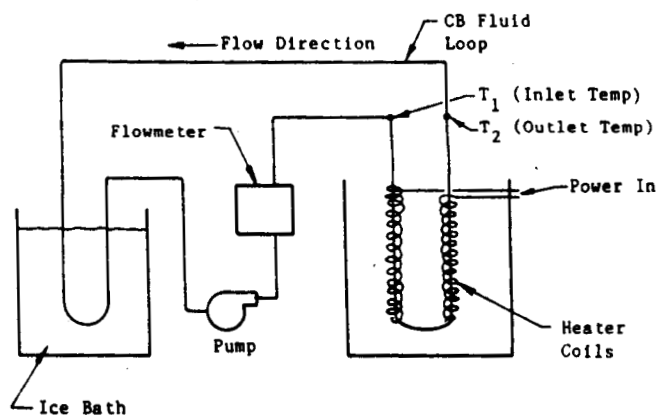


Figure 5 Schematic of Lockheed In-House Flow Calorimeter

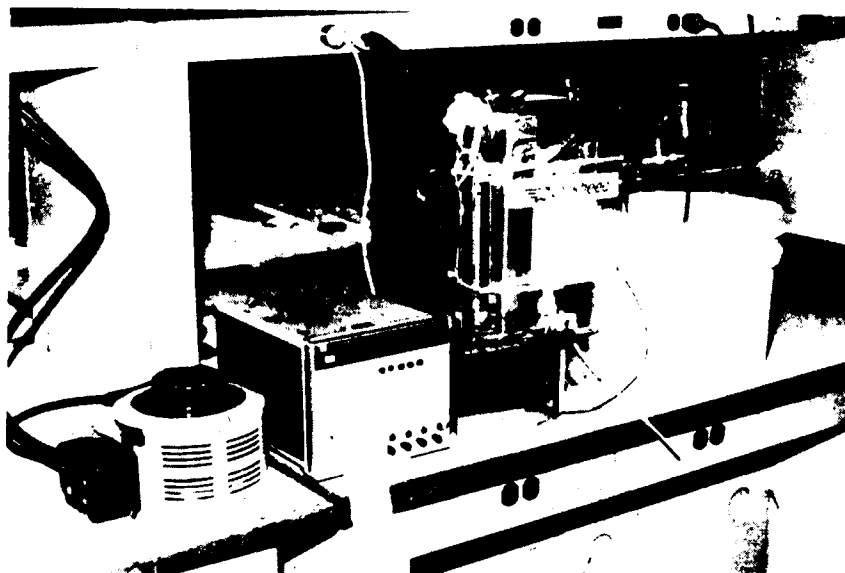


Figure 6 Photograph of Test Flow Calorimeter

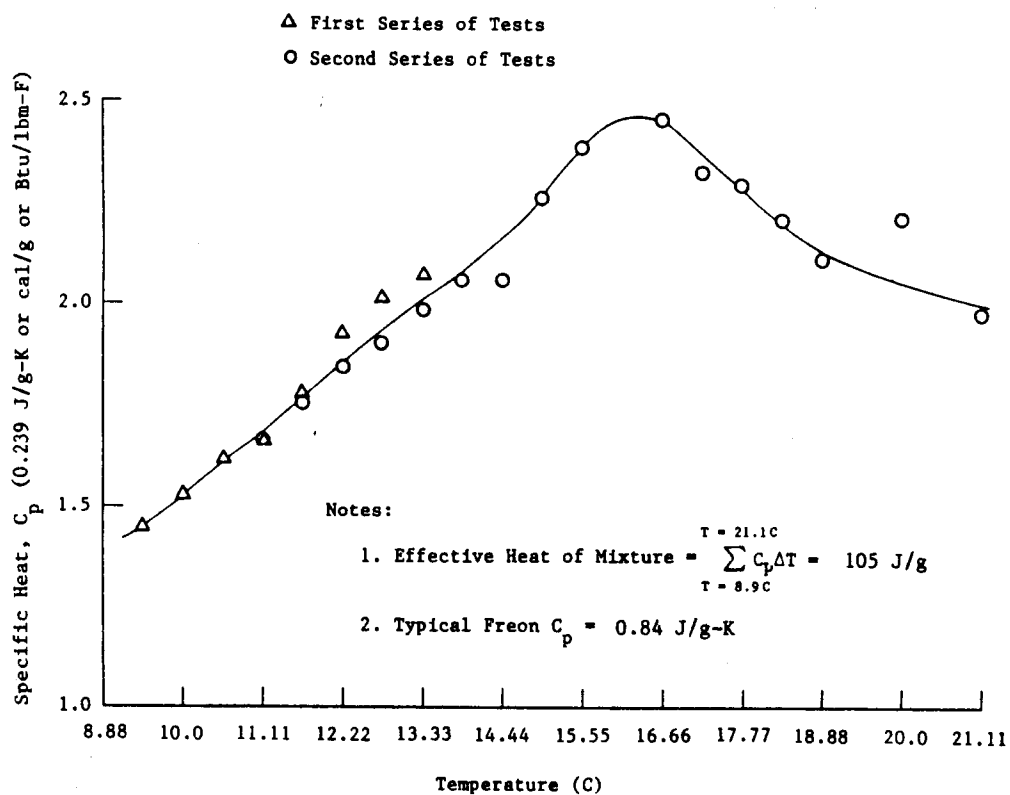


Figure 7 C_p vs Temperature for Triethylamine (TEA)/Water CB Near the CST (Solution: 32 Wt% TEA, 68 Wt% Water)

Note: Bath liquid feed and return ports are actually in front and back of the flasks rather than to the side as shown.

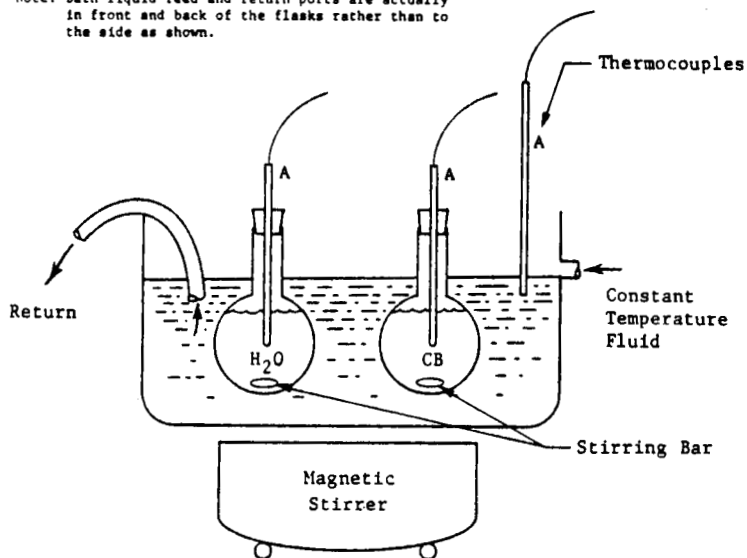


Figure 8 Test Set-Up

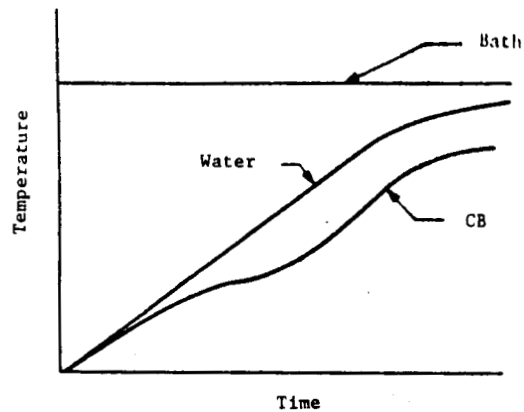


Figure 9 Water-CB Comparison

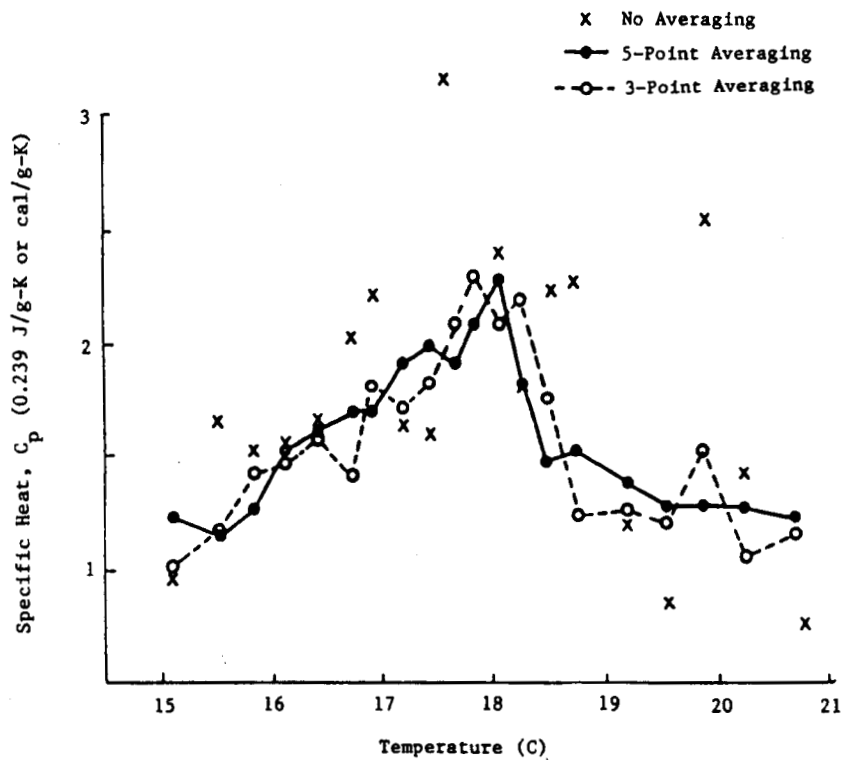


Fig. 10 C_p vs Temperature - Data Obtained for a 37.9 Percent Triethylamine (TEA) - Water CB With and Without an Averaging Procedure